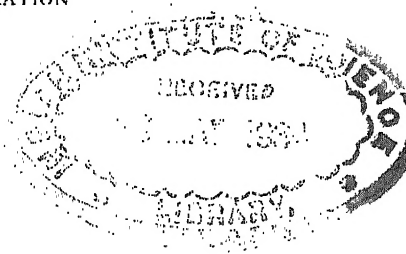


THE
INDUSTRIAL DEVELOPMENT
OF
SEARLES LAKE BRINES
WITH EQUILIBRIUM DATA

BY
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and
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AND CHEMICAL CORPORATION



American Chemical Society
Monograph Series



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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is difficult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's *Handbuch der Organischen Chemie*, Richter's *Lexikon*, Ostwald's *Lehrbuch der Allgemeinen Chemie*, Abegg's and Gmelin-Kraut's *Handbuch der Anorganischen Chemie* and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coördinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of coöperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

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Preface.

This book has two purposes. First, to add to the record of scientific literature certain phase rule diagrams and data. This information was necessary to the work at Trona; it belongs to the American Potash & Chemical Corporation, was done at their initiative and was paid for with their money. It has now largely served its original purpose, and normally would have spent the rest of its existence buried in their files. The American Potash & Chemical Corporation in consenting to the publication of these data has performed a courteous act. One could wish that other chemical corporations would likewise release data from their files when it can be done without furnishing ammunition to direct competitors. Scientific information is about the only valuable commodity we are accustomed to bury for fear someone else might derive benefit from it.

The second purpose of the book is to give a short story of the application of research, technology and common sense to the development of a potash and borax business. This story of the diagnosis of a situation in an industry and the course of development which led to success is not such an uncommon thing; in fact it is all in the day's work, so why write a book about it? The answer lies in the very peculiar attitude that was manifested toward the development of a potash industry in this country. During the World War potash was news. Anyone could be sure of making the front page by talking about potash and how this country was becoming independent of Germany. With peace came a change. College professors, bankers, business men, chemists and ministers of the Gospel now granted interviews freely to prove that this country could not hope to produce potash successfully in times of peace. Many of the interviews, possibly inspired, were circulated by a well known advertising agency. The opposition to American potash was apparently deep seated, based on faith and belief rather than on facts or logic. Few things are more aggravating and often harmful than loud and dogmatic assertions that a given thing cannot be done, coming from people who obviously are in no position to judge whether it can be or not. I think we all react to this in much the same way; we look back of the loud speakers to see who is broadcasting; that tells us who is

most afraid that the thing will be done; then we proceed to do it. The plant at Trona undertook to manufacture two staple products, potash and borax, in competition with two world monopolies. To-day it has by far the largest borax plant in the world, and one of the largest potash plants. This was accomplished without governmental assistance from tariff or otherwise, and the business is profitable and still young. Since the record that it could not be done was so voluminous it seems well to make note of the fact that it has been done.

This book does not contain detailed descriptions or processes, nor scale drawings of apparatus. The former are not so antiquated nor the latter sufficiently obsolete to permit their publication yet. Anyone intelligent enough to use that kind of information will know better than to expect it here.

My associates really include all the men who actually contributed to the manufacture or marketing of the products, or to research, or to design and construction of the plant. Many of their names will be found on the pages in connection with specific parts of the work. But it was an organized piece of cooperation in which it would be difficult and probably useless to evaluate just what each one of us contributed, beyond saying that we saw it all and were a part of it.

JOHN E. TEEPLE.

New York City,
July, 1928.



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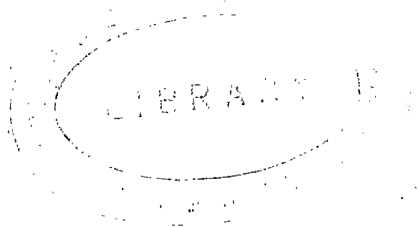
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PART I.

History and Development.

CHAPTER I.

SEARLES LAKE.

We are concerned in this book with natural brines and deposits of very soluble salts. It is obvious that these deposits can form only in comparatively dry climates where evaporation exceeds precipitation, and it is just as obvious that they can be found today only in equally arid regions unless they happen to be protected from access of water by impervious layers of clay, hardpan or stone. So we find the sodium nitrate deposits of Chile, the sodium sulfate of Arizona, the salt lakes of California and Nebraska, the Great Salt Lake of Utah, and the Dead Sea, all in comparatively dry climates and all having salt deposits unprotected from the weather. The salt domes, however, of southern Louisiana and eastern Texas are capped with an impervious layer of stone so that they still persist even in those relatively wet climates. Likewise the potash deposits of Germany and Alsace are thoroughly protected by layers of stone or impervious clay.

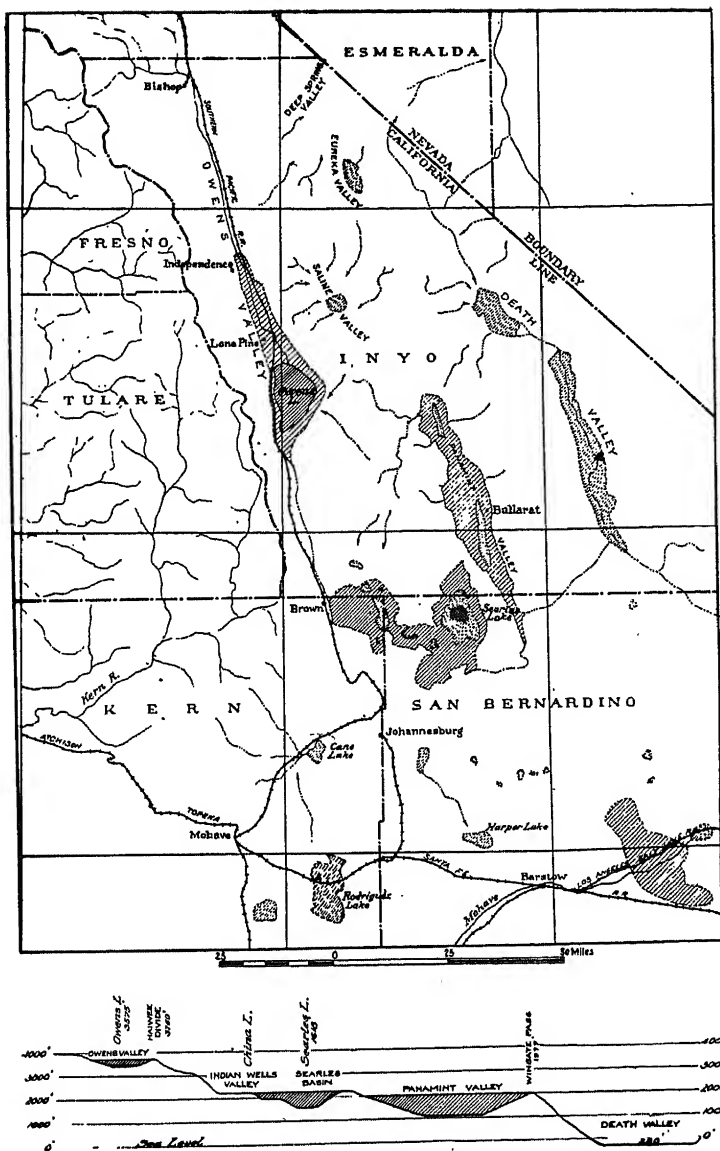
While these deposits of soluble salts seem large, sometimes having a magnitude of billions of tons, they are relatively small and unimportant accidents, mere short circuits in the much larger scheme of things. We may regard the whole earth as one gigantic Soxhlet extractor surrounded by a spherical condenser. Vapors are continually rising from water wherever this solvent appears on earth, turning to rain at the condenser, falling with a very unequal distribution and disintegrating the earth, channeling and worrying it into solution. Each bit of falling water carries its load of dissolved matter back to the great extract, the sea. Someone has computed the amount of extracted salts still remaining in solution. If the ocean were evaporated to dryness it would furnish a block of solid salts large enough to cover the whole United States and one and a half miles in depth. From the time water starts to dissolve material until the solution reaches the sea it undergoes many

vicissitudes of solution, precipitation, resolution and change. The surface waters start with a relatively large proportion of sulfates and carbonates and a small amount of chlorides. When we examine the sea, however, we find a very small amount of sulfates, much less of carbonates, and a large amount of chlorides, because the carbonates and sulfates have largely gone to form the insoluble masses of limestone, dolomite, magnesite and gypsum.

We search the world for pockets of segregated salts to be exploited for our use. We find a billion tons of Epsom salts deposited in the eastern arm of the Caspian. We find half the salt of the Dead Sea is magnesium chloride. We find the caliche beds in Chile, a soda lake in Africa, potash beds in Europe and maybe in Texas, and salt deposits throughout the world. These are matters of importance to us because they serve our needs, but when we compare them with the four and a half million cubic miles of salt contained in the sea it is apparent that they are only accidental pockets, however important they may be to us. It is the function of the geologist to try to reconstruct the past history of these pockets. The business of the chemist has to do solely with their future. The questions that the chemist propounds to himself are: What is in this deposit? Does it contain something that the world now needs? Can I separate it in a form that is marketable, and can I profitably deliver it at the market at a price that the world is willing to pay?

Searles Lake in California is just one of these pockets. It lies about 185 miles northeast of Los Angeles in a valley probably twenty-five miles long and ten miles wide. This valley has the Argus Range of mountains closing it in on the west and the Slate Range on the east. Beyond the Slate Range to the northeast is the Panamint Valley; beyond that the Panamint Range, then Death Valley, and then Funeral Range (see map). West of the Argus Range is Indian Wells Valley, and further to the north Owens Lake and valley. A few thousand years ago all these valleys formed one group of lakes and connecting rivers.* Searles Lake then covered about four hundred square miles and overflowed at a point over six hundred feet above its present surface, the overflow being about twenty-two hundred and fifty feet above sea level. To-day the residue of this lake covers about eleven or twelve square miles, its surface being only about sixteen hundred feet above sea level. The lake now is a shallow basin of salts still saturated with their mother liquor. The salt body covers the whole eleven square miles to a depth of fifty to seventy-five feet, and below this is mud and slightly soluble or insoluble carbonates of calcium and magnesium and sulfates of

* See U. S. Geological Survey Bulletin 580L.



MAP SHOWING RELATIVE LOCATION OF SEARLES LAKE AND ADJACENT VALLEYS.
 BOTTOM SHOWS COMPARATIVE LEVELS WHEN THEY COMPOSED ONE
 UNITED SYSTEM. From U. S. Geol. Survey Bull., 580 L. C.

calcium for over five hundred feet more. The small body of salts is still saturated with mother liquor. In the winter after rains the liquor may be two or three inches above the top of the salt body, and in the dry season it may be two or three inches below it, giving a total annual variation of only four or five inches in the level of the brine. During most of the year the surface of the salt is dry and hard so that an automobile may be driven over it with entire safety.

This shallow pan of salts and brine is all that is now left of a lake that was once nearly forty times the area and twenty times the depth. The total annual rainfall in the immediate vicinity of the lake is only from three to seven inches, but is probably somewhat more on the mountains. No surface waters reach the lake excepting occasionally after a cloudburst or freshet, but underground waters are flowing to it continually from the mountains and the upper part of the valley, and wells sunk four or five miles north of the lake usually have no difficulty in furnishing plentiful supplies of slightly brackish water. Surrounding the lake body on nearly all sides is a naked playa. In the winter it is an alkaline slippery mud composed of sand, a little clay, and weak brine. In summer it is a thin crust whitened by the alkaline salts that have been left by evaporation. Breaking through this crust, however, reveals the slippery mud only a short distance below. The region around is a desert—interminable sand with a scattering vegetation of greasewood, desert sage, occasional thistles, desert holly and cactus. In the background all around the naked gray mountains close the scene, gray excepting in spring when the whole desert may be carpeted for a few days with brilliant but short-lived desert flowers.

So far as we know, the whole body of salt in this shallow basin of crystallized salts and brine is composed of five definite materials—

1. Halite (NaCl)
2. Trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$)
3. Hanksite ($9\text{Na}_2\text{SO}_4 \cdot 2\text{Na}_2\text{CO}_3 \cdot \text{KCl}$)
4. Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)
5. Glaserite ($3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$)

We originally supposed that there were other salts in the crystal body, such as sodium bicarbonate and sodium sulfate, either in the form of thenardite or mirabilite, but none of these is in equilibrium with the brine, and so presumably none of them exists to-day in the salt body. There is a possibility that one other salt may exist. This is burkeite ($2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$). It will be seen that this salt is somewhat allied to hanksite, and under ordinary laboratory conditions of handling the brine burkeite is the product that appears where you would expect

hanksite. Only by prolonged efforts with much coaxing over many months has it been possible to reach the stable hanksite equilibrium instead of the metastable burkeite one, so it is not impossible that similar conditions may exist in parts of the lake giving rise to the presence of this sixth phase. The temperature of the lake is apparently just within the lower limit at which the formation of burkeite is possible.

An examination of the five or six constituents of this vast salt body reveals only two metallic elements, sodium and potassium, and only four acid groups, chloride, sulfate, carbonate (and bicarbonate) and borate. This is the most remarkable thing about the salt body. There are plenty of calcium and magnesium salts in the mud below the present lake, there is a collection of calcium carbonate pinnacles to the south of it, there are crystalline deposits of magnesium sulfate and aluminum sulfate in the mountains just across the Panamint Valley to the east of it, there is limestone to the north of it, but in this whole billion cubic yards of crystallized salt there is only sodium and potassium.

There seems to be no particular uniformity in the distribution of the five components of the salt body whether we examine it by vertical or horizontal sections. Many test wells have been sunk to obtain samples of the salt and of the brine at different levels below the surface. We will give a record of one of these wells sunk near the center of the lake about fourteen years ago. Average samples of the salt were obtained for every five-foot section. Adhering mother liquor was not entirely removed. The salts were separated from the mud which is sometimes present in small amounts and sometimes forms a layer of as much as five or six inches, and the dried salts were then analyzed, the analysis taking no account of insoluble matter. This work was done long before our equilibrium studies enabled us to determine what salts were actually present, so that the results are somewhat formal in their character, all potassium being represented as potassium chloride, all sulfate as sodium sulfate, all carbonate as sodium carbonate no matter whether it was originally present as carbonate, bicarbonate or trona.

The record is given just as it was determined at that time. We know now that only two of the five salts listed here, that is sodium chloride and borax, were actually present as such in the salt body. We know now that the brine of the lake is not in equilibrium with sodium carbonate, sodium bicarbonate, sodium sulfate or potassium chloride. Interpreting the figures, however, in the light of our present knowledge we see that the first three sections representing the top fifteen feet are essentially sodium chloride, with a small amount of adhering brine.

COMPOSITION OF SALTS AT DIFFERENT LEVELS IN ONE WELL

No.	Depth feet	NaCl per cent	Na ₂ CO ₃ per cent	Na ₂ SO ₄ per cent	KCl per cent	Na ₂ B ₄ O ₇ per cent
1	0-5	98.17	0.57	0.31	0.43	0.21
2	5-10	98.09	.66	.24	.24	.17
3	10-15	96.93	1.51	.59	.27	.14
4	15-20	80.06	7.24	11.04	1.51	.51
5	20-25	8.14	14.17	72.16	4.82	.88
6	25-30	17.42	16.11	50.40	4.04	12.14
7	30-35	34.22	28.68	26.19	2.92	8.46
8	35-40	62.42	20.14	14.78	1.75	1.34
9	40-45	57.54	15.82	12.50	4.78	9.61
10	45-50	52.88	10.86	20.63	7.03	8.06
11	50-55	31.64	14.33	35.86	14.12	4.55
12	55-60	9.69	4.45	50.98	34.35	.87
13	60-65	36.22	24.36	33.58	5.23	.31
14	65-70	12.82	65.67	15.56	4.26	1.38
15	70-75	16.68	39.54	13.66	5.21	24.92

The fourth section is still 80 per cent sodium chloride, the remaining 20 per cent being hanksite and trona. The fifth section is about 90 per cent hanksite, about 8 per cent sodium chloride, with a little trona. The sixth section is about 60 per cent hanksite, probably 17 per cent sodium chloride, 12 per cent borax (this would represent over 20 per cent crystal borax) and 10 per cent trona. The respective amounts of these salts change from section to section, until in the ninth we have the first appearance of a new salt, glaserite, and the twelfth section represents probably 60 per cent glaserite and about 35 per cent sodium chloride. Number 14 is probably over 60 per cent trona, and the bottom section of the salt body, over seventy feet below the surface at this point, contains trona, borax, salt and hanksite. All of the test wells are alike in showing the top fifteen or twenty feet to be nearly pure sodium chloride, and below that level varying mixtures of the five component salts. Any other well will show the same salts present but with entirely different distributions.

The table on page 17 gives the contemporary analysis of brine from each five-foot level in the same well. When examining these figures it should be remembered that both potassium chloride and sodium borate are consistently given a little higher than our analyses would show to-day. Field methods for potash determination were probably not so accurate as those we have now; and the borax figures recorded include phosphate. It will be noticed that the brine at the surface contains more sodium chloride and less of all the other constituents than any lower levels do. After about the forty-foot level it becomes fairly uniform. The last line of the table contains an analysis of the brine below the forty-foot level in this same part of the lake

COMPOSITION OF BRINE IN SAME WELL

No.	Depth feet	NaCl per cent	Na ₂ CO ₃ per cent	Na ₂ SO ₄ per cent	KCl per cent	Na ₂ B ₄ O ₇ per cent	Total Solids per cent
1	0-5 }	20.36	2.76	3.61	2.83	1.08	30.70
2	5-10 }						
3	10-15	18.02	4.09	4.67	4.14	1.38	32.45
4	15-20	16.74	4.39	6.63	4.26	1.49	33.54
5	20-25	16.81	4.39	6.71	4.17	1.48	33.70
6	25-30	16.68	4.37	6.74	4.33	1.60	33.77
7	30-35	16.15	4.48	6.77	5.05	1.60	34.01
8	35-40	15.86	4.64	6.83	5.40	1.60	34.44
9	40-45	15.78	4.73	6.67	5.47	1.56	34.32
10	45-50	15.71	4.80	6.69	5.59	1.60	34.38
11	50-55	15.84	4.83	6.65	5.37	1.60	34.32
12	55-60	15.77	4.80	6.65	5.45	1.65	34.45
13	60-65	15.65	4.81	6.66	5.66	1.63	34.41
14	65-70	15.63	4.87	6.69	5.64	1.59	34.45
15	70-75	15.85	4.87	6.64	5.55	1.64	34.38
Present Brine		16.36	4.86	6.85	4.74	1.50	34.38

as it appears to-day. Comparison shows that excepting for the error in the original analysis which consistently made potassium chloride too high and sodium chloride too low, there has been no real change in the brine in fourteen years. As we move out toward the shores of the lake, however, other test wells show smaller percentages of potassium chloride, some containing only one-half or one-third as much as the above figures show. I once thought of the lake as a beautiful natural equilibrium vessel, but it has a number of serious defects. The temperature of the deep brine is fairly uniform at 22.5° C. summer or winter. The composition at any particular spot varies but little with the rainfall. There has been plenty of time for equilibrium to be reached. The one thing that is lacking, however, is an efficient stirring mechanism. The continual inflow of large but varying amounts of subsurface water and the continued outflow of water by evaporation from the surface cause an unfortunate lack of uniformity in the different parts of the lake. Since we do not know just where the underground waters enter the lake, nor what course they follow before they reach the salt body, it is difficult to predict just where the richest potash and borax brines will be found. We only know that it will be at a very considerable distance from any shore, and probably over forty feet below the surface.

The brine contains both bicarbonate and metaborate. It is usual, however, to include these in the figures for carbonate and borate unless for special reasons the separate information is required. Percentage of Na₂B₄O₇ as recorded indicates the total B₂O₃ of the solution computed to Na₂B₄O₇. The analyses given above account for practically 100 per

cent of the salts in the salt body and 99 per cent of the salts in the brine. The remaining 1 per cent may be ignored until one is operating a concentrating process in the plant; then it often becomes a matter of great importance to know where these minor constituents are accumulating and what is their final disposition. The following rather complete analysis made in 1925 probably shows all the inorganic constituents which are present in more than spectroscopic traces.

COMPOSITION OF SEARLES LAKE BRINE
Specific Gravity 1.30 at 70° F. (21° C.)

Salt	Per Cent by Weight	Pounds per Gallon	Grams per 100 Grams of Water	Mols per 1000 Mols of Water	Molar Weight
NaCl	16.50	1.787	25.30	38.97	116.92
Na ₂ SO ₄	6.82	0.739	10.46	13.25	142.06
KCl	4.82	0.522	7.39	8.93	149.12
Na ₂ CO ₃	4.80	0.520	7.36	12.51	106.00
Na ₂ B ₄ O ₇	1.51	0.164	2.32	2.07	201.28
Na ₃ PO ₄	0.155	0.0168	0.238	0.261	164.04
NaBr	0.109	0.0118	0.167	0.101	205.84
LiCl	0.021	0.0023	0.032	0.068	84.80
Na ₂ S	0.020	0.0022	0.031	0.072	78.06
As ₂ O ₃	0.019	0.0021	0.029	0.026	197.92
CaO	0.0022	0.00024	0.0034		
Fe ₂ O ₃ & Al ₂ O ₃ ...	0.0020	0.00022	0.0031		
NH ₃	0.0018	0.00020	0.0028		
NaI	0.0014	0.00015	0.0021		
Sb ₂ O ₃	0.0006	0.00006	0.0009		
Total solids (approximately)	34.782	3.76807	53.339		
Water by difference	65.22	7.063	100.00		
	100.00	10.83	153.34		

Even as small a percentage as that of sodium iodide represents 60,000 pounds of iodine per year entering into plant liquors. Then there would be, say, 100,000 pounds of white arsenic, another 100,000 pounds of lithium chloride, 6,000,000 pounds of bromide, and maybe 10,000,000 pounds of trisodium phosphate.

Oxidizing the brine before precipitation increases the apparent sodium sulfate content by about 0.12 per cent. A part of this increase represents the sulfide sulfur, some is probably organic sulfur, and some more may be dissolved sulfur or polysulfide or sulfarsenite, or something else. The brine contains organic matter and has some odor and slight color.

It should of course be remembered that the above analysis represents a certain sample of brine taken from a particular spot on a definite

day. A different sample, time or place would show a different result. In the above analysis we have also recorded the pounds per gallon, grams per hundred grams of water, and mols per thousand mols of water, because these figures will be useful for reference later in the discussion.

Earlier in the chapter we mentioned four questions that a chemist asks of a natural deposit. To the question "What is in this deposit?" we have given the answer above. To the question "Does it contain something that the world now needs?" the answer is "Yes". There is a demand and a steady market for every one of the fifteen or sixteen constituents listed, as well as for other combinations such as potassium sulfate, potassium bromide, carbonate, iodide, etc. The third question "Can I separate any of these twenty or so materials in a form that is marketable?" the answer again is "Yes". Any good chemist can separate any one of twenty different materials here and prepare it in the shape that is marketable. This leaves only two basic questions. Fourth, "Can I profitably deliver any one of these at the market at a price that the world is willing to pay?" This question has been answered "Yes" in the case of two products, potassium chloride and borax, and there will probably be a positive answer ultimately in the case of one or two more products, but I would call your attention to the fact that questions 1, 2, and 3 are very primary and casual questions compared with 4. The fifth question, which is really a part of the fourth, is "How shall I do it?" and some of the data in relation to this takes up the remainder of the book.

CHAPTER II.

EARLY HISTORY.*

The Searles Lake region has attained national prominence on at least three different occasions; first, soon after 1860 on account of its silver and gold mines; second, some twenty-five or thirty years later on account of borax production; and third, still another twenty-five or thirty years later on account of potash. The Modoc Mine in the Argus Range to the west of Searles Lake, the New York Mine in the Slate Range to the east of it, and the Panamint Mine in the Panamint Range to the northeast were all well-known silver and gold mines during the early California days, and Ballarat, Skidoo and Panamint City were typical mining towns of the period. In order to transport the products from the mines and the supplies to the mines an extensive freight system with mule teams was organized. The route led from Panamint City and other places to the north of the lake, past the present city of Trona down the west side of the lake and on to San Pedro or Los Angeles. This transportation system lasted for many years.

Among the early miners who came to the region were John W. Searles and his brother, Dennis Searles. John W. Searles was supposed to be familiar with Teal Marsh in Nevada where borax was being produced on a commercial scale, and he noticed the similarity between that source of borax and the playa on the west shore of Searles Lake. Analysis of the white efflorescence confirmed this suspicion and Searles and his associates built a small experimental plant on the west side of Searles Lake about three miles south of the present town of Trona. The results of the experimental plant were apparently satisfactory because in 1873 six hundred and forty acres of placer claims were located in Sections 20 and 21 at the northwest corner of the lake near the present town of Trona, and within a few years other locations brought the total to over two thousand acres. The lake at that time was known as Slate Range Lake. During 1873 a group of miners on the east side

* The information in this chapter covering the period before 1919 was furnished largely by Mr. S. W. Austin. Mr. Austin examined Searles Lake in 1908 and before that had been Register of the Land Office for the District in which Searles Lake is located. In 1909 he was appointed Receiver for the California Trona Company and has maintained a connection with that company or its successors ever since, being at present in charge of the Los Angeles office of the American Potash & Chemical Corporation.

of the lake organized the Borax Lake Mining District, and the lake itself afterwards took this name, until finally on account of the activity of Searles it became Searles Lake. In 1878 the group of borax producers on the west side of the lake incorporated as the San Bernardino Borax Mining Company with John W. Searles as president, manager, and two-fifths owner. Considerable development work was then done in the way of piping in water from the mountains, and a larger and more permanent plant was built on the ground between the present town of Trona and the lake. Searles was apparently a very forceful character and kept the Indians in rather definite fear of him. He was also progressive. He occupied one of the canyons, from which water was drawn for the plant, developed the springs, planted trees and vines of a semi-tropical character, and apparently made it a veritable garden spot, evidences of which still appear to-day after many years of neglect. He was successful in developing the borax business. The operations were comparatively simple, consisting merely of leaching and crystallizing, but the business of getting the material to market and developing a market required a considerable exercise of sound judgment. It was still necessary to haul the borax to market by mule teams, and it was his foreman, "Salty Bill" Parkinson, a noted mule skinner of the region, who drove the twenty-mule team at the St. Louis Exposition in 1904 which made that trade mark famous.

In 1895 the San Bernardino Borax Mining Company was sold to the Pacific Coast Borax Company. The plant was closed and operation then ceased on Searles Lake because the buyers preferred to derive their borax from the colemanite deposits in Death Valley and elsewhere. No further activities on Searles Lake appear until 1905 or 1906 when it began to be investigated as a source of soda ash. By 1908 nearly the whole lake had been located, and the California Trona Company was organized with a capital of one million dollars to manufacture soda ash on a large scale both from the brine and from the extensive reefs of trona along the eastern side of the lake. This company purchased what was left of the property of the San Bernardino Borax Mining Company, its plant, buildings, bunk houses, shops, and water rights, and leased the land. The company borrowed considerable sums of money to finance its undertakings, but before approaching any point of production it was in such financial difficulties that a receivership ensued in 1909. The receiver attempted to keep the property intact and continue the necessary assessment work, building roads which would give access to the salt body, sinking exploration wells at different parts of the lake to determine distribution of brine and salt, and fighting off

rival parties who were trying to jump the claims. One of the invading parties comprised about forty men, including engineers and gun men, and required the presence of a United States marshal to suppress it. The only net result of the claim jumping was to cloud the title, but this title was finally cleared in 1916 through a judgment which recognized the California Trona Company's claims and invalidated those of the invading parties.

In February of 1913 the Government withdrew the whole of Searles Lake as a potash reserve. At that time the California Trona Company held claims amounting to twenty-six thousand acres, but as exploration work proceeded and the character of the lake was more clearly developed the less advantageous claims were dropped one by one until finally, in 1918, when the assessment work had been completed and the Government patented to them a clear title to their claims the amount they actually asked for and received was three thousand three hundred and twenty acres to the north of the center of the lake. The rest of the body of the lake was promptly leased by the Government to eight or ten different interests for the production of potash, but none of these leaseholders has ever produced potash in commercial quantities.

It is not clear when the occurrence of potash in Searles Lake was first reported, but it is known that analyses made as far back as 1898 show its presence. In 1910 and 1911 during the receivership under Mr. Austin the lake was sampled and analyzed for at least three different interests besides the owners. So far as we know all four of them reported the presence of potash. By 1912 the presence of potash here was so well known that it came to the attention of the Government, and the United States Geological Bureau sent representatives to investigate and published a bulletin on the subject. This bulletin attracted a great deal of attention. It was well written and widely read. Of course it had no influence on the production of potash at that place because the only ones who have ever produced potash at Searles Lake commercially were quite well aware of the situation before the bulletin was published. What it did do was to persuade a number of people to secure leases from the Government on unowned parts of the lake and then wait for someone to finance them or buy them out. Some of them were partly financed but the net result was nothing.

By 1912 the California Trona Company had in hand as the result of all investigations a voluminous report on the utilization of the brine for the manufacture of potash, borax, soda ash, and sulfate of soda. The general method was the one which seems to make an appeal to almost any chemist the first time the problem is proposed to him, *i.e.*,

carbonate the liquors and so remove all of the sodium carbonate as sodium bicarbonate or trona. This is filtered off and calcined to make soda ash. The filtrate is then subjected to successive evaporation, filtration and crystallization steps to obtain potash, borax and sodium sulfate, all dependent of course on the fact that the solubility of potassium chloride increases very much with temperature, that of sodium chloride remains almost stationary, and that of sodium sulfate has a definite curve that does not coincide with either.

The voluminous report was probably unduly optimistic; the operations can be performed in the laboratory and the separations made, without any question, but from a commercial point of view one can see that the report failed to take account of a good many rather important factors. The people who were interested in the California Trona Company and in the money that had been advanced to it were very expert in mining matters, but not particularly strong on chemical manufacture. Therefore they could not be expected to foresee the difficulties, but they did take the very sensible step of passing the report to a very well-known firm of consulting chemists for confirmation and advice. Unfortunately the report of this firm likewise was unduly optimistic, with the result that the American Trona Corporation, which by this time had been organized to take over all the assets of the receivership, as successor to California Trona Company and the bondholders, determined to build a preliminary plant to operate the process on a small scale at Trona. By the end of 1914 the plant was finished on the same site that had been occupied by the California Trona plant, and before that by the San Bernardino Borax Mining plant, and the Trona Railway, about thirty-five miles long, had been built to connect the plant with the Southern Pacific Railroad at Searles station. Then the plant started on its preliminary run. Something went wrong. I do not know just what, nor have I been able to find any report or record in the archives. There apparently is nothing but tradition to rely on. Something went wrong. The trial run was never finished, the plant was abandoned, the process given up, and several hundred thousand dollars had disappeared—a total loss.

This might seem to be an excellent opportunity for criticism, but I have none to offer. The company officials had apparently made careful investigation, and so far as they could learn had selected suitable men for the work and given them the facilities for carrying it out. The original proposer of the process and the plant had apparently done the best he knew how after careful investigation. The consultants had gone through a novel and difficult problem, had carried out the different

steps themselves on a small scale and found nothing to prevent successful operation. Notwithstanding, the thing had not turned out well. All three parties to the transaction had been mistaken. But this is not an unusual situation even with the best of men and of corporations. It is cited here because it is typical of what so often occurs during the birth of a new enterprise or a new development. The problem at first looks simple, delightfully easy, just as this problem did, and almost any chemist would have undertaken it with a feeling of confidence and a sense of merely taking a short stroll before breakfast through a pleasant path in the woods. Soon the path begins to meander, obstructions arise, detours must be made, and before he realizes it his simple path has become a complicated maze of bypaths all apparently leading nowhere, and instead of being a peaceful stroller he has become a desperate struggler. The ones who do not die here keep on struggling until they finally emerge on good roads leading in a definite direction and things are again perfectly simple. This is the natural course of almost any novel enterprise, and this development of a potash industry is no different from the others. In 1912 it was strolling. There were a number of paths and they all looked straight and easy. In 1919 when I first saw it it was still struggling, and now in 1928 it is on clear highways. All the participants in the incident related above have ceased any connection with the potash industry long ago and so the tale may be used to point a moral. The moral is, don't underestimate the difficulties of a new enterprise, and the fact is that we probably will the very next time a new enterprise presents itself. My only criticism begins at the point where the plant failed. There was no record of what happened. At that point there could be nothing to represent all the money that had been spent excepting information, and the information was not recorded.

Various other processes and combinations of processes were suggested, considered, reported on, tried, and finally a real plant was built at Trona which began commercial operation in September, 1916. At about the same time a combination of the Pacific Coast Borax Company and the Solvay Process Company also started operation in a commercial plant at Borosolvay. Both of these plants produced potash throughout the period of the war, and they are the only plants on the lake that have ever succeeded in getting to what would be called commercial operation for potash. The Borosolvay plant closed down about the end of 1920 and has never since reopened. The plant at Trona, now owned by the American Potash & Chemical Corporation, has operated continuously since it first started in 1916 excepting for a period of ten months from May, 1921, to April, 1922. During this ten-month period

production was stopped but research and development continued. A discussion of the various processes used or proposed, probable and improbable, will be postponed until we have before us some data on which a judgment can be based.

During all of 1917 and 1918 the production of these two plants at Trona and at Borosolvay was a very important factor in ameliorating the situation caused by the absence of foreign potash during the war. The potash manufactured was of rather low grade; it was contaminated with various materials some of which might have been harmful. It would be absolutely unsalable in the market to-day. The plants were inefficient, wasteful, and costly to operate, but on the other hand the demand greatly exceeded the supply, there was no sales problem, and the prices were extraordinary. Before the war potash in the form of muriate had become rather stabilized in price at 75¢ to 80¢ per unit. During the war it was \$7.00 to \$8.00 per unit, which apparently offered a very comfortable margin of profit to the operators in spite of their very inefficient plants and methods. Of course it offered little or nothing in the way of real profit because actually, as history shows, they should have been amortizing the entire cost of their plants over the period of two or three years only, during which they could operate.

At the armistice and during the months immediately following there was a very rapid drop in price, so that by the middle of 1919 potash could be bought for from \$1.75 to \$2.00 per unit. Probably no plant in America could then make the product at that price if it gave due consideration to depreciation and amortization or obsolescence. This naturally caused a considerable turmoil in the whole industry. Companies who thought they were highly prosperous in 1918 manufacturing potash, a commodity which was a prime and permanent necessity, now suddenly found themselves faced with staggering monthly losses, and in the case of the two plants at Searles Lake they also had to meet the difficulty of a market which demanded a higher quality of goods than they had been able to furnish. The year 1919 then marked the turning point for most of the plants which had built up the American production of over 50,000 tons of K_2O per year. Only two courses were open to them; either to succumb, or to make a scientific and technical study of their problems such as they should have made in the first place. Most of them elected the former procedure; it was easier and less expensive to die. The one at Trona chose the latter, and is selling its potash to-day at about 70¢ per unit without any particular difficulty, in competition with the Germans and the French.

CHAPTER III.

SOLUBILITY AND DOUBLE SALTS.

It is obvious that any recovery of potash from a brine such as that at Searles Lake must involve concentration, that is, an increase in the percentage of potash either in salts or in liquor in relation both to water and to the other salts. The two plants operating on the lake had learned that they could get such an increase in percentage of potash in the brine by triple-effect evaporation at sufficiently high temperatures. This removed water by evaporation and salted out sodium carbonate, sulfate and chloride. The resulting concentrated liquor when cooled precipitated a salt rich enough in potash to market during the war, but it was known that considerable quantities of potash were lost with the waste salts. It was even known that the presence of sodium carbonate or mother liquors had some influence at times on the amount of potash that was lost in this way. Since, however, potash was known to be lost in three different ways, it was very difficult to get accurate figures from plant operation. First, the liquor foamed very badly in the pans and carried over potash to the condensers or to the belts of the other pans; second, potash in some combination apparently became insoluble in the liquors and actually precipitated along with the sodium chloride and sulfate; and, third, there was great difficulty in freeing the waste salts from the adhering liquors which were rich in potash. Consequently recoveries were comparatively small. An examination of the analysis figures given previously indicates that at a minimum it is necessary to evaporate about $13\frac{1}{2}$ pounds of water and separate and discard about 6 pounds of other salts in order to recover 1 pound of dry potassium chloride. In good triple-effect evaporation we expect to evaporate about 2.2 pounds of water from 1 pound of steam, so that we would expect to use a little over 6 pounds of steam to recover 1 pound of potash.

Burning fuel oil of, say, 150,000 B.t.u. per gallon in a boiler house of reasonable efficiency we might expect to produce 120 or 130 pounds of steam from a gallon of fuel oil. Combining these figures we get a theoretical result of 100 gallons of fuel oil required at a minimum to furnish the steam needed for evaporating the water from 1 ton of potassium chloride if we have complete recoveries. Needless to say there

are no 100 per cent operations in a plant. Actual practice does not approach very close to this figure. Actual consumption during the war period was probably nearer 1000 gallons per ton of potash than it was to the theoretical 100. I have frequently seen it well over 1500. This consumption of several times the necessary amount of oil for evaporation could apparently be materially reduced by three different lines of attack, in addition of course to the ordinary improvements from increased efficiency in machinery. First, to stop the foaming in the pans and consequent loss of potash from entrainment; second, to improve the separation and washing of waste salts and thus prevent loss of potash adhering to these salts in the form of brines on which work had been done; third, to study the equilibrium conditions in the pans themselves and so avoid the possibility of the liquors becoming saturated with some potash salt and precipitating it among the waste salts. The first two problems seemed to be essentially questions of plant operation. The third one very clearly demanded long laboratory study of solubilities, in terms of the layman, or of phase rule application in terms of the chemist. Perhaps it would not be out of place here to give the impression received in 1919 as quoted from a report which I wrote at that time:

"Your fundamental questions here are questions of relative solubility, and the influence of certain salts on the solubilities of other salts.

"You have present only sodium and potassium combined as carbonates, bicarbonates, chlorides, sulphates, metaborates, and biborates, and at nearly every step of any process you have ever used or may use in the future, you are dealing with a solution that is saturated with respect to some one of these compounds, and so is salting it out; or you are dealing with a solution which is unsaturated with respect to one of them, and so is dissolving it.

"Before you began any operation or process six years ago, then, your natural course would have been to study these solubilities; to make solubility curves covering the range of temperature between, say, -20° C. and 110° C., and covering all reasonable variations in concentration of the individual constituents. Any good physical chemist could have done this for you. With such information in hand you would be able to discuss any possible process intelligently. Without it you are entirely at sea. Notwithstanding the fundamental importance of such information for your work, I cannot find that any effort was ever made to obtain it until within a week or two of my visit to Trona. The work done in that last week or two was only preliminary, probably inaccurate,

and covered only a couple of arbitrary conditions of the many possible ones; but notwithstanding, I gathered a more intelligent basis of judgment from these few curves than from any other single source at the plant".

The above comments on lack of proper research work, when taken by themselves, may seem a bit rude and forceful, but in my experience clients desire to be told the plain truth. The statements would have been just as true regarding any other potash plant in America. For that matter many other industries besides potash fall into the same error. To act first and do the considering afterward is rather typical of pioneer work, and America is still largely a nation of pioneers in business. A beautiful example came to my attention only a few years ago. We were all familiar with the roadside scene of a flat tire, a hand pump, and a man bathed in perspiration and profanity. An inventive genius, seeing these scenes often, conceived a brilliant business idea. Sell everyone a cylinder of compressed gas to carry in the car. No more hand pumping. Simply connect the gas cylinder to the tire, turn a cock, the tire is inflated, disconnect, and drive on. Now carbon dioxide is cheap, very compressible, and a small cylinder will hold a lot of it. There you have the idea on which an enormous business could be built. The next steps were patent application, company organized, financed, plant production arranged, cylinders bought, literature prepared, and then, apparently not till then, someone tried it. Alas, a rubber tire will not hold carbon dioxide. That gas is just about as effective for inflating tires as water is for filling a sieve.

Naturally when I was invited to take some responsibility in rejuvenating the American Trona Corporation and in making my own recommendations effective, an intensive study of the equilibrium of the constituents in Searles Lake brine was one of the earliest tasks. The work began in 1919 and continued intermittently, as data were needed, through several years. This was a utilitarian study. An accuracy of 0.3° C. was maintained. In analyses the accuracy required was usually 0.3 per cent of the total. The limits of temperature checked were 20° to 110° C., and only those systems and those temperatures were studied which might throw some light on our problems of manufacture. The industrial man feels called upon to place rather definite limits about his research activities, while the scientist in pure research may roam gaily over any field that attracts him.

The methods used in equilibrium study can best be indicated by referring to Diagram 1. Two hundred cc. of water and an excess of sodium chloride are placed in a 500-cc. rubber-stoppered bottle and

rotated in a thermostat for about 16 hours. Then the salts are allowed to settle and a sample of the clear liquor sucked through a cotton plug into a pipette, weighed and analyzed. The remainder of the mixture is rotated for another day and analyzed again. This is continued if necessary until samples taken on successive days check showing that equilibrium has been reached at 36 grams NaCl per hundred grams water or its equivalent 55.5 mols Na_2Cl_2 per thousand mols water. This locates point 239 on Diagram 1, plotted in mols per thousand mols of water. It shows the solubility of NaCl in water at 20°C . It is a univariant point in the two-component system $\text{NaCl}, \text{H}_2\text{O}$, with three phases present—solid NaCl, solution and vapor. Our interest throughout lies in the univariant points and in the divariant lines connecting them. A determination of the temperature and concentration at the nonvariant point in this system— $\text{NaCl}, \text{H}_2\text{O}$ —where the fourth phase, ice, appears, might be of great importance elsewhere but does not particularly concern us here. At a univariant point with one degree of freedom we expect the number of phases present to exceed the number of components by one, but in our work water is always one of the components, and solution and vapor are always two of the phases, all the other phases being solids. It will be simpler, then, to remember that at all univariant points throughout this work the number of solid phases equals the number of solid components, *i.e.*, components other than water. Having determined univariant point 239 in a system having one solid component we add successive small amounts of sodium carbonate and analyze the solution from day to day. We now have two solid components and are searching for univariant point 2 with two solid phases present—NaCl and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. This is finally located at a concentration of 33.6 mols Na_2CO_3 and 39.1 mols Na_2Cl_2 per thousand mols water. A determination of point 237, the univariant point for $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ with one solid component, then the approach to point 2 by additions of NaCl, enables us to check the above concentration. Having located point 2 we make successive small additions of Na_2SO_4 to the mixture, thus approaching point 4. Now there are three solid components and we expect to find three solid phases at point 4. They prove to be NaCl, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, and $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$, a new double salt which we have called burkeite. The concentrations at point 4 are checked by approaches from points 3 and 246. In general a univariant point with two solid components is located by approach along two divariant lines, one with three solid components along three divariant lines, etc. When all the univariant points in Diagram 1 have been determined in this way, and the divariant lines connecting them

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are plotted, we have the solid figure representing all the possibilities of the four-component system, NaCl , Na_2SO_4 , Na_2CO_3 , H_2O , at 20°C . The plane of each pair of axes represents one of the three possible three-component systems bounding three sides of the four-component one. And the lines used as axes represent the three bounding two-component systems. Every one of the 60 diagrams given later represents either a complete four-component system at a given temperature or a part of a five-component one. Information regarding two- and three-component systems must be sought in the appropriate four-component diagrams and data sheets.

The important constituents of Searles Lake from our point of view are the sulfates, chlorides, carbonates, bicarbonates, borates and metaborates of sodium and potassium, or Na , K , H , SO_4 , CO_3 , B_2O_4 , Cl , H_2O , a seven-component system. A complete study of this would include

8 systems of		6 components	
25	"	"	5
39	"	"	4
32	"	"	3
12	"	"	2

and there are of course several other components of interest in the lake besides these seven, such as phosphates, arsenates and bromides, for example. All of the twelve two-component systems listed above have been adequately studied long ago as can be seen from any handbook or table of solubilities. The same is true of many of the three-component systems. The information we needed, however, related chiefly to systems of four and five or more components, and this was almost a virgin field so far as concerns the particular group of salts in Searles Lake. The little that had been published was by van't Hoff, D'Ans, and Blasdale, and covered only one four-component system (the chlorides and sulfates of potassium and sodium). The three investigators were not in entire accord with each other on that one system. The data given in the following pages will be found to cover 25 four-component systems, 6 five-component systems and 1 six-component system at a few selected temperatures. In the case of the five-component ones of course only parts of each system are given, and some of the systems include other components than the seven listed above. With each added component it becomes increasingly difficult to make a diagram which will convey information, and if a diagram does not help to clarify a set of data or express it in a better form than the numerals do, then why make it? When it comes to diagrams illustrating systems of 6 or more components I am inclined to think that the ordinary worker puts more

information and energy into the making of the diagram than he can possibly recover from the use of it.

The work of accumulating information necessary for the study of the 32 systems recorded in this book could not be considered romantic; in fact at times it must have made a near approach to drudgery, being lightened only by the fact that it was necessary, and that it gradually shed light on our problem. The chemists having the different pieces of work in charge were, of course, supplied with competent analysts to relieve them as much as possible. During the first few years of the work Mr. R. W. Mumford was in charge of research and development. By training and experience he was primarily a chemical engineer, and while he and I both understood fully the necessity of this equilibrium study and were ready to furnish every sort of opportunity, sympathy, and general advice to the men actually doing it, neither of us was especially well equipped to give the detailed assistance which the workers needed. The man best fitted to do this by training and experience was Mr. W. E. Burke, and so by unanimous consent that became his job. The first six systems were worked out primarily by Mr. Harald de Ropp, usually working alone. The work was, however, new to Mr. de Ropp, and Mr. Burke was so helpful in shaping its general course that I feel I only do him justice in crediting these systems to Burke and de Ropp jointly. Some of the other systems Mr. Burke worked out alone, and others were actively directed by him when he became head of the research department. In fact he played such an important part in the study of every system that was studied that his name will be found either as the sole worker or as a co-worker connected with every one. A number of other systems have naturally been studied during the course of the investigation, but some of them have not yet entirely served their purpose and so are not yet ready to be released.

It would probably be appropriate to list here the double salts encountered in this equilibrium work. They are—

1. $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$, trona, sesquicarbonate of soda, long known and frequently described in the literature. Searles Lake brine is in equilibrium with trona, which occurs as an important constituent of the salt body, particularly in lower levels. It also occurs above the salt surface level of the lake in the trona "reefs" near the northeastern and eastern shores. From these reefs some thousands of tons have been mined and marketed without purification for use as an impure but very cheap alkali.

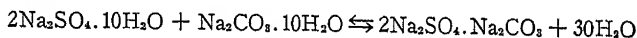
2. $3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$, glaserite, aphotitalite, also long known and frequently described. It is in equilibrium with Searles Lake brine and

occurs in the salt body in important amounts, especially below the 50-foot level. Glaserite is in equilibrium with a solution of its component salts, Na_2SO_4 and K_2SO_4 , at ordinary temperatures, but is not below about 0°C . With KCl and Na_2SO_4 the transition point is between 4° and 5°C . below which glaserite is not stable.

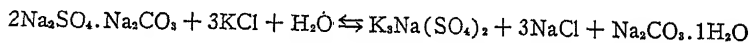
3. $9\text{Na}_2\text{SO}_4 \cdot 2\text{Na}_2\text{CO}_3 \cdot \text{KCl}$, hanksite, well known but not of frequent occurrence. It contains about the same percentage of KCl as the Searles Lake brine does with which it is in equilibrium. It forms an important part of the salt body where its characteristic crystals are often large, well formed, and easily recognizable. Hanksite is apparently stable in the lake at 22.5°C ., but is decomposed by water at 25°C . or above, and on warming the solution precipitates burkeite, $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$. The temperature range within which hanksite may exist is seemingly very narrow. The hanksite equilibrium is exceedingly difficult to reproduce in the laboratory, requiring great care and patience and weeks of time. This has been accomplished, however, as will be seen from System VI, Diagram 17, but the extreme slowness and difficulty of formation makes hanksite unimportant in plant practice, where its place is always taken by burkeite.

4. $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$, burkeite, a new double salt discovered by Mr. W. E. Burke in 1919.* Although its native occurrence has not hitherto been reported, and although it does not seem to be a constituent of the Searles Lake salt body, we fully expect to hear of it from Owens Lake, or some of the other alkaline lakes, now that attention has been called to its existence. For this reason, and also as a matter of convenience in referring to a material formed in the plant at the rate of some thousands of tons every week, we have given it a name, burkeite.

In the reaction



the transition point is about 25°C ., the burkeite being stable above that temperature. Another reaction of vital importance in plant operation is the one connecting burkeite and glaserite:



The transition temperature is about 49°C ., glaserite being stable only below that when in contact with the solution.

Burkeite forms beautiful crystals of very high luster and is stable in equilibrium with Searles Lake brine under plant conditions at all temperatures from 20° to 110°C .

* *J. Ind. Eng. Chem.* 13, 249 (1921).

5. $\text{Na}_2\text{CO}_3 \cdot \text{K}_2\text{CO}_3$. Several hydrates of this double salt have been reported, but no mention seems to have been made of the anhydrous salt. We show $\text{Na}_2\text{CO}_3 \cdot \text{K}_2\text{CO}_3$ in the diagrams of Systems IV, V and VI, and under the conditions of these diagrams, 35° or over, the salt in equilibrium is not hydrated.

6. $\text{K}_2\text{CO}_3 \cdot 2\text{KHCO}_3 \cdot 3\text{H}_2\text{O}$. This salt is mentioned by Rammelsberg and its probable occurrence indicated by others. The conditions under which it forms are shown in System XIII.

7. $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$. This is a new double salt of sodium metaborate and sodium chloride discovered by Mr. Burke in 1920. If Searles Lake brine could evaporate to dryness naturally, and at each stage be separated from its precipitated salts, large quantities of the B_2O_3 and NaCl would be precipitated as this double metaborate chloride. In the research reports this double salt had also been given a name in "honor" of an individual. In fact that is the fate of all new products. Research men have an uncanny knack of selecting some characteristic of the new salt which forms the basis for a personal name, not always complimentary to the individual "honored" if the real facts are known. It seems wiser to abandon mineralogical names excepting for products of known natural occurrence, or those whose discovery in the native state may be anticipated in the immediate future. When Searles Lake dries up, a few thousand years from now, we shall need a name for this double salt.

8. $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$. This is a new sodium metaborate-trisodium phosphate double salt, discovered by W. A. Gale and C. F. Ritchie in 1924. It may be prepared by dissolving a mixture of trisodium phosphate and sodium metaborate in hot water and allowing to cool slowly. Varying proportions of the constituents do not change the composition of the precipitate; it is a true double salt. It has also been observed to crystallize from a solution of disodium phosphate and sodium metaborate, and even from a mixed solution of trisodium phosphate and borax. It forms tetragonal crystals, specific gravity 1.628, only slightly soluble in water at 0°C ., but it melts in its own water of crystallization at about 69°C . Like the preceding double salt this metaborate-phosphate would be in stable equilibrium with Searles Lake brine at the end point of crystallization.

9. $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{AsO}_4 \cdot 36\text{H}_2\text{O}$. A metaborate arsenate, prepared in the same manner as No. 8 and isomorphous with it. This double salt does not appear in the following diagrams. It was prepared by Gale and Ritchie in 1924.

Of the nine double salts listed above, four (Nos. 4, 7, 8, 9) were dis-

covered in the course of the work; three others (Nos. 3, 5, 6) had never appeared in an equilibrium diagram before. One other double salt that was anticipated did not appear. This is sulfohalite, $3\text{Na}_2\text{SO}_4 \cdot 2\text{NaCl}$, whose occurrence as a mineral in the Searles Lake region was reported in 1900.

CHAPTER IV.

EARLY PLANT OPERATION.

On my first trip to Trona to make a report on the plant in 1919 I found it equipped with triple-effect evaporators of a type very commonly used in the manufacture of sodium chloride from brine.* These evaporators were probably suitable for salt manufacture but they were very poorly adapted to the concentration problems at Trona. Moreover, they were arranged in a very peculiar and unusual manner. One double effect, theoretically used as a preheater, fed liquor into a triple effect for further concentration, and on the other side a single effect fed liquor into another triple effect. This arrangement was evidently not in the interest of economy. The brine in the pans foamed like soapsuds, which was not particularly the fault of the evaporators, and in order to keep this foam under control it was customary to blow live steam at times into the second or third effects; also not economical. A brine of this type depositing large quantities of salts requires rather vigorous positive circulation through the heating tubes, but these pans were equipped with a type of propeller which used nothing stronger than moral suasion, and the liquors were of such an unregenerate type that moral suasion was not effective. Because of the slow circulation, the tubes salted up very rapidly and frequent stops were necessary for washout. Due to some of the minor constituents in the brine the tubes of the first effect were frequently found coated with an impervious and insoluble enamel which so cut down the heat transmission that frequent resort to mechanical violence was necessary to remove it. This enamel corresponded roughly in composition to a lithium sodium ammonium phosphate, and its removal naturally shortened the life of the heating tubes. When the brine is heated it gives off ammonia which renders the use of any material containing copper inadvisable. It also gives off carbon dioxide in very considerable quantity which causes air binding in the next effect. A third material in the vapors is hydrogen sulfide and possibly sulfur in other forms, which corrodes the outside of the heating tubes in the next effect, causes a deposition of iron sulfide, iron oxide, and elementary sulfur. This of course again cuts

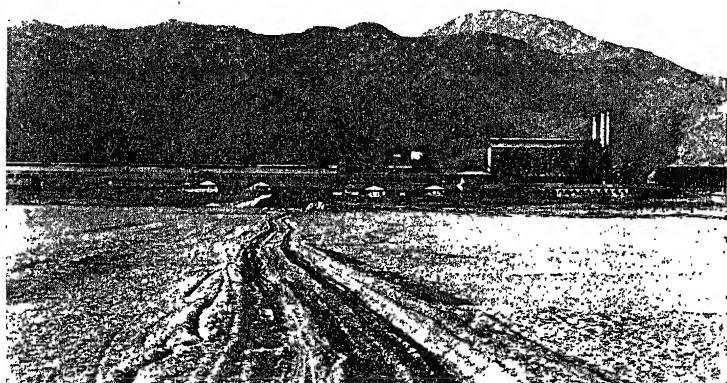
* Described in *J. Ind. Eng. Chem.* 10, 839 (1918).

down the heat transmission and shortens the life of the heating tubes. The discarded salts were removed from a boot at the bottom of the pan by bucket elevators, and then more or less inefficiently washed, all of which tended to produce very heavy losses. It was clear that the equipment as it existed was not well adapted, but it was also probable that no other standard equipment would prove very suitable for the special case before us, and so it seemed wise to analyze the problem step by step and see what could be done by making changes to the equipment as it existed.

To consider some of the evaporation problems for a moment, probably the most serious one was foaming. We are all familiar with this phenomenon in commercial evaporation and there are several well-known methods for handling such liquors, but I have never seen such pernicious, persistent and aggravating foam in a regular operation. At times the condenser water was actually richer in potash than the raw brine fed to the pans. Unless this could be controlled either the losses of potash from partly evaporated liquor would be enormous, or the pans must be operated at such a slow rate that production would be negligible.

In my first report I find the following comment: "At present in the plant they are adding a small amount of oil to the pans to cut down the foaming. This, too, is a tradition. I did not find out who started it, on what theory it was based, or what work had been done to indicate whether it was beneficial or not". The use of oil on foamy liquids is very common and often effective, but why in this case use only an amount which was entirely inadequate? Why not add a proper amount to control the foam, rather than simply tease it? I asked the people in authority at the plant and the oldest operators. No one knew, or rather everyone knew but their explanations did not agree or did not sound reasonable. A majority felt sure, from tradition, that it would not do to add more oil, and they were right, as traditions often are. One may have great respect for traditional conclusions but they are not entirely satisfying, so at a later date when we had small laboratory pans for studying the problem a trial of the oil showed that there was no foaming so long as a thin film remained on the surface. This film tended to disappear but a further addition of oil sufficient to keep a film always present kept the foam under complete control, evaporation proceeded at full speed and there were no obvious disadvantages; score—experiment 1, tradition 0. The experimental result was exactly what one would expect, so we next started a full-size single-effect evaporator in the plant with instructions to run it at top

speed and make sufficient additions of the oil to keep a slight film always present on the surface and control foaming. This was done, and for several hours that pan had no trouble with foam, and produced high-grade concentrated liquor at a rate never before seen by the awed beholders. The operation was a complete success—in the evaporating house—but the patient died in the crystallizing house. After about twenty-four hours spent in excavating filters, centrifugals and other equipment which seemed buried under layers of concrete, the plant resumed operations, and we knew why you should never add enough of that oil to stop foaming.



VIEW OF PLANT LOOKING WEST ACROSS THE PLAYA.

I have mentioned that burkeite forms sparkling crystals of very high luster. The film of oil acts as a flotation agent and selects the burkeite crystals for attachment, then floats them over with the concentrated liquor to the crystallizing house where the mixture of crystal and oil sets like concrete. Tradition was finally right, without the faintest idea why.

In studying the question of foaming it seemed reasonable to suspect organic matter in the brine as the cause. Synthetic brine containing all known constituents excepting organic matter could be evaporated without difficulty. Natural brine after treatment with absorbent carbon like Darco no longer foamed. In searching the watershed for organic-matter which might be responsible I selected greasewood as the probable source. The leaves of this very common plant appear as if coated with a varnish, easily soluble in very dilute alkalies, and a very small addition of this

solution to a synthetic brine produces an excellent imitation of foamy natural brine. Probably a number of different organic materials are responsible, and more recent work at the plant by W. A. Gale indicates that the organic matter may be sodium salts of humic acid, and that its function is probably foam stabilization rather than foam formation, because its removal has little effect on surface tension.

We found many substances which would prevent foam, such as cholesterin, capric acid, pine oil, turpentine, rosin, turkey red oil, and amyl alcohol, most of these being impracticable for use under vacuum evaporation. Finally R. W. Mumford worked out a practical one.* The way to control this foam is to add soap or a fatty acid. This ended foaming as a serious trouble and made it certain that we should use steam evaporation and not be compelled to resort to solar evaporation or some other makeshift.

Another serious difficulty was the maintenance of proper vacuum. In any evaporating pan the amount of heat transmitted from the condensing steam to boiling liquor is approximately proportional to the difference of temperature between the two. If the steam is 10° C. hotter than the liquor a certain amount of evaporation occurs, while if it is 20° hotter than the liquor we have practically twice as much evaporation, other things being equal. If the effectiveness of a single pan is proportional to this drop in temperature then the effectiveness of a set of pans such as a triple effect, other things being equal, is proportional to the total temperature drop between the condensing steam which heats the first effect and the vapor which goes to the condenser from the last effect. If the steam to the first effect has a temperature of, say, 210° F., *i.e.*, about atmospheric pressure, and the vapor leaving the last effect to go to the condenser is at 90° , we have a working drop of 120° , which will divide itself between the three pans according to their respective coefficients of heat transmission and heating area. But suppose we are evaporating a material like brine, which has a boiling point 20° or more above the temperature of the vapor it gives off. Then in the three pans of a triple effect we would lose over 60° of our working temperature, leaving us less than half of our 120° range. To carry the idea farther, suppose in the evaporation of water we have only 60° difference between the incoming steam and the outgoing vapor. This would do very well for water and would give us 20° drop to each pan, which would produce effective evaporation. In case we were using this brine, however, this 60° difference would be entirely absorbed by

* U. S. Pat. 1,591,725.

the excess boiling temperature over water at the same pressure and we would have absolutely no evaporation at all.

Now in the plant as it existed in 1919 the vacuum was maintained by a rotating mechanism which was naturally very subject to erosion, and to make matters worse some of the parts contained copper in the composition which is very subject to the action of ammonia in the vapors. New equipment would start with a very respectable vacuum but in a matter of days this would fall to a level which was quite unsatisfactory. Substitution of proper barometric condensers and the removal of all copper from the system solved this first difficulty. The brines contain bicarbonate, and in the vacuum pans a considerable part of this is decomposed to carbonate, evolving carbon dioxide. This makes the removal of non-condensable gases a more serious problem than one ordinarily encounters. So-called air-binding was a very frequent difficulty. The steam belts of the evaporating pans were very large and the gases tended to collect in pockets, the net result being to reduce very largely the effective heating surface. It was only by long periods of trial and change that all these pockets were located and effectively drained of gases.

The foaming in the pans affected the vacuum in two ways. First, directly, because one of the common methods of controlling the foam when it got too bad was partially to break the vacuum until normal boiling was resumed. This not only acted directly to slow down evaporation but indirectly it introduced still larger amounts of non-condensable gases. The second action of the foam was to cause serious friction in the vapor lines, particularly in the vapor line going from the third effect to the condenser, so that the pressure and temperature in the third effect were very considerably higher than they were at the condenser. This caused a loss in the effective vacuum and consequently a loss in the working temperature drop. The change in condenser, introduction of more and colder water to it, control of foaming and control of non-condensable gases enabled us to keep a satisfactory vacuum, and finally raising the pressure at which steam was fed to the first effect gave us a satisfactory working temperature, but there apparently is no way to avoid that 60° loss of working temperature due to the increase in boiling points of the brines.

A very important part of any evaporation problem is the transmission of heat, usually through the wall of a tube, from the steam on one side to the liquor on the other side. The evaporating calandria in the plant at Trona contained a grand total of about 25,000 tubes, each 6 feet long by 2.5 inches in diameter. Placed in their favorite position

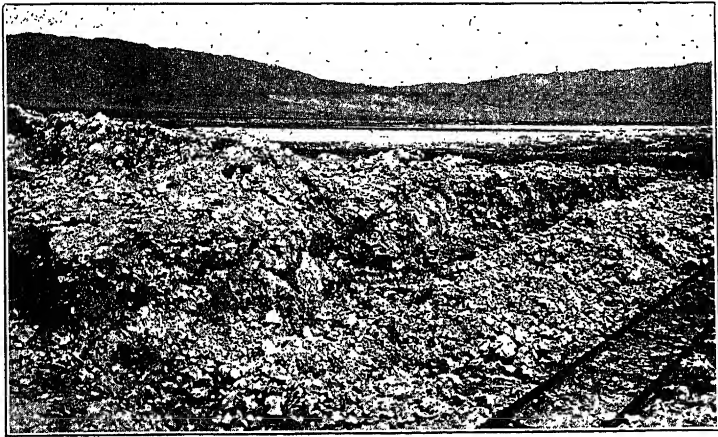
of end to end this made about 30 miles of tubing, through whose walls heat must be transmitted from the steam on the outside to liquor on the inside. This makes about 100,000 square feet, or 2.5 acres of heating surface, enough if properly designed and distributed to supply a very large part of the potash used in the United States. But in 1919 this mass of tubing was producing only a little over 1 ton of KCl per day per linear mile.

In transmitting heat through a given surface there are four factors which may have a tremendous influence. One, a deposit of soluble salts on the walls, what is known as "salting up" of the evaporator. This is bound to occur whenever one is evaporating concentrated liquors which are precipitating salts. Rapid circulation of the liquors may delay the effect, but eventually, usually within a matter of hours, the heat transmission has been reduced so much that the heater must be stopped while the salt is washed out. Second, formation of scale from the evaporating liquors. In most liquors this scale consists of insoluble calcium salts, but in the case of Searles Lake brine there is no difficulty at all with the calcium and there was no formation of scale in any pans, if we except the lithium sodium ammonium phosphate enamel previously mentioned which often formed in the hottest pan. When this enamel has once thoroughly set, hot or cold water has little influence on it and mechanical violence must be used. If taken in hand before it has become too hard it could, with care, be removed. This enamel has a very low coefficient of heat transmission and when it has once formed the effective action of the evaporators is very much reduced. We never did learn the exact conditions of temperature and concentration which led to its formation, and while it caused a great deal of trouble over a long period of time it finally, through some change in temperature or concentrations, rectified itself and is no longer a serious cause of worry. The third factor is the corrosion of the tubes on the steam side. In our case this corrosion took the form of oxide and sulfide of iron. This also slows down the heat transmission very rapidly, besides of course shortening the life of the tubes, and the arrangement of the tubes in the calandria was such that access to them for purposes of cleaning was very difficult. The fourth factor is the speed of flow of liquor through the tube. A higher rate of speed not only keeps the tubes clearer of salts but increases the actual heat transmission per square foot.

We could not accomplish a great deal in improving conditions for any of these four factors in the then existing plant. What we could do was largely palliative. We did finally succeed in getting a production of about 3.5 tons KCl per linear mile of tube per day, but the real

solution of the problems did not come until several years later when a properly designed plant was built in which the production is approximately 12 tons KCl per mile per day; but that is another story which will be taken up later.

In the production of potash from this brine it should be remembered that for every ton of potassium chloride made at least six tons of waste salts must be removed from the evaporators, washed free of adhering concentrated or partly concentrated liquor, and discarded. This is not an easy task. The equipment we found at the plant, consisting of bucket elevators, classifiers and settlers, was not very effective, and



A REEF OF SODIUM SESQUICARBONATE OR TRONA, THE MINERAL THAT GAVE ITS NAME TO THE TOWN.

in addition it entailed heavy maintenance charges and frequent stoppages. It was replaced by another system which worked a good deal better and caused less trouble, but since that one too has now gone into the discard it need not be discussed further here. It was the custom to filter all concentrated liquor and this operation required quite a battery of filters and their attendant operatives. It seemed useless to filter a liquor which would settle readily if given an opportunity, so the filters were discarded. In an evaporating plant such as this it is good practice to use the steam for power before it goes to the evaporators for heat, and usually the plant is laid out so that there is a balance between the steam that goes to the prime movers for power and the steam that goes to the evaporators. This plant was laid out with that idea in mind, and because the evaporators were expected to

take large quantities of steam some of the prime movers were direct-connected turbines, which consequently ran at low speed and took enormous quantities of steam. Unfortunately, as indicated above, the plant could not do the evaporation that it was designed to do, consequently there was a great excess of steam going to the prime movers which the evaporators could not afterward use, and which was exhausted into air. This was an obvious matter that was corrected either by changing the type of turbine or alternately driving by electric motors, which balanced the steam so far as heat and power were concerned, but it introduced one added difficulty. Electric power came to the plant over a single line through many miles of desert. If anything happened to stop the power for more than ten or fifteen minutes evaporation must stop immediately and the evaporators must be emptied before they froze solid.

The next serious difficulty was pumps. All liquors that we handle are saturated and frequently contain suspended salts, so that on the slightest provocation a pump is liable to freeze. Unfortunately the insides of the pumps used in most cases were inaccessible. I wish someone who has spent a good deal of a lifetime in factories struggling with pumps would write a book about them, and I urge every young man aspiring to be a chemical engineer to make a profound study of pumps in the relation of their construction to the type of material they must handle and the type of duty they must serve. In this one plant at Trona we are probably pumping about 150,000 gallons of water or brine every minute and it becomes a matter of great economic importance. We gradually replaced all liquor pumps by ones that could be easily inspected and cleaned in case of difficulty, and saw that the important ones were in duplicate. These are more or less routine matters and they are mentioned here only because it is in this part of his problem the chemical engineer is most likely to make his errors.

In the crystallizing house, by 1919 the plant management had learned the principle involved in separating potash from borax in concentrated liquors. Borax is sluggish and tends to form supersaturated solutions. So if a mixed solution is cooled rapidly, not agitated and not seeded with borax crystals, the potash may be crystallized and removed before the borax precipitates. The principle was known but practice had not been developed to a point which would give what we now consider a marketable potash, *i.e.*, considerably less than 0.5 per cent borax present. In developing the cooling plant the designers had probably overestimated the importance of rapidity of cooling and underestimated the effect of agitation and seeding, consequently the

coolers were very complicated, equipped with coils for cooling water, other coils for refrigerated brine, and even still other pipes in which ammonia could be expanded directly. These coolers went through several stages of development, mainly in the direction of simplification, and each step improved the separation and reduced the amount of refrigeration required. To-day we use no more refrigeration machinery to turn out 250 tons of potash per day than was originally used for 20 or 25 tons.

From the equilibrium data given in Part II we know now that our problem is to pass from the concentration indicated by the triangle in Diagram 17 to a spot near point 137 in Diagram 21, without precipitating any potash or borax. This was not known in 1919, and although the concentration was headed in that general direction it stopped very far short of point 137. The product then averaged about 60 per cent KCl or less. As our experience and information increased the concentrated liquor was improved and to-day the aim is to have all potash salts between 95 per cent and 98 per cent KCl.

In this general way production and research moved hand in hand, sometimes one leading, sometimes the other. Recording thermometers, pressure gages, flow meters and weirs of all kinds were tried in an attempt to determine just what occurred during the operations. The whole plant was subject to experimental operation and gradual change of unsatisfactory equipment. This is never a desirable thing to do. A plant should operate uniformly and the place for experimental work and development is normally entirely outside of the producing plant. But in the present case the course adopted was necessary because the research and development work had not been done first, and because the plant was there, was not functioning properly, and experimental operation combined with research was the quickest way to determine just what was happening and what should be done about it.

By May, 1921, this period was over, various changes noted above had been made in equipment, and some measure of technical control had been established. Tests of the remodeled equipment and methods indicated that we had a plant which could be tuned up with experience to a fairly uniform daily production of 100 tons KCl and 50 tons borax per day, both perfectly marketable. The costs of production would not be all that could be desired, but on the other hand they were not prohibitive. It was evident that continued study would enable us to develop a thoroughly attractive and successful business. It was further evident, at least to me, that what in July, 1919, had been only a fair bet, just a project well worth trying on account of the large amount of money

already involved, was now a most excellent prospect with the odds all in its favor. Just one thing might ruin it, and that is the thing that has caused and is causing the failure of many otherwise sound enterprises—impatience, discouragement and disbelief on the part of the stockholders and directors. It takes time and patience as well as money, and such development work is no place for a man who wants everything done yesterday. It is only fair here to say that in this case the stockholders were unfailing in their support throughout, to their own very substantial financial gain.

The plant closed for ten months about May, 1921, but research and development work continued without decrease or interruption. The plant reopened in March, 1922, as an operating, not experimental, unit and has continued ever since, excepting for a little interference in 1926 due to construction of the enlarged plant.

The first step in operating the reopened plant in 1922 was to tune it up to the expected production, which was accomplished; and the second was to concentrate attention on uniformity of product and operation, and reduction of costs, which was also successful. The third step had to do with sales. During and after the war selling was easy. If it were rumored that you had goods for sale buyers fought for the privilege of taking them away from you. Many a clerical order taker in those days developed the idea that he must be a wonderful salesman. By 1922 selling had become an art requiring action again, and our much increased production needed to be moved regularly. So we brought in Mr. A. A. Holmes as sales manager and definitely organized that department. His first duty was to make friends of the consumers, and his second one was to convert the seasonal demand for potash, to which consumers had been accustomed, into a steady daily outflow from the plant which our production department needed. There was the usual difference in point of view between selling and operating departments because neither, naturally, ever quite fully understands the troubles and difficulties of the other. The sales department always wants to sell what it can sell easiest, and the operating department always wants to make what it can make easiest and cheapest. Unfortunately these two desires do not always coincide, but personal conferences two or three times a year between the heads of the two departments usually smooth out all differences and result in satisfactory compromises where neither gets quite all that he wants. In general my attitude is that while a plant is in the struggling stage, trying to work out its major production problems, the burden is on the sales department to sell what the plant can make, if it is at all salable. After this period is over the burden

is on the plant to make what the sales department can sell, within reason.

By the middle of 1924 research, development, production, sales, and income were all progressing so smoothly that it was time to lay rather definite plans toward applying the information and experience we had gained and were still gaining toward the design and construction of a larger plant, and one more nearly suited to the work. It was ultimately decided to convert the existing plant, which could make about 100 tons KCl and 50 tons of borax per day, into one producing about 250 tons KCl and 125 tons borax per day, a part of the latter to be converted into boric acid, but this is a story for another chapter.

CHAPTER V.

SPECIAL FEATURES OF THE PROBLEM.

Aside from the fixed charges incurred in obtaining ownership and in developing the 2500 acres of salt body in the lake, the only cost of raw material for the plant is the cost of pumping. Any basis for depletion charge which might become effective within a generation is very difficult to figure. Amortization of cost of the property should be accomplished well within the life of the plant, but in fact this amortization becomes a daily and not a per gallon charge, and we are left in the very peculiar situation of being able to disregard the amount of raw material used. Whether we obtain a 20 per cent or a 100 per cent recovery of the potash and borax in the brine used means little to us, a few cents per ton at most, so long as the losses are confined to raw brine on which no real work has been done. In evaluating mother liquors to see whether they should be discarded we can select a datum level of about 5 per cent KCl and 3 per cent borax. Anything below that level would naturally be discarded at once as worse than valueless. Anything richer than that has a value only equivalent to its excess content above the datum level minus any detriment or disadvantage from impurities that may be incurred by its use. This value also may easily be negative and the liquor should be discarded. I stress this point because chemists are so often urged to conserve resources and save everything, as though 100 per cent yields and no waste products were a sort of religious slogan that would pave the way to heaven. I can't agree with that point of view at all. A chemical plant is not a place for collecting and keeping family heirlooms on account of the sacred memories attached to them; it is a place for making things, and the best way to make things is by judicious waste of the unimportant so that you have room and time to devote entirely to the thing you are making. If there are those whose consciences might be hurt by such waste they may be reassured in this case, for all discarded materials are thrown directly back into the lake, just like little fishes, and so saved for posterity.

Since cost of raw material may be neglected, the heaviest operating charges are fuel for heat and power, first, and labor second. When it required many hundreds of gallons of fuel oil to produce one ton of

potash, fuel was a far more important item of cost than it is to-day. It is not surprising, then, that many experiments on solar evaporation were made in the effort to cheapen production. In fact no one can view that expanse of desert with cloudless skies, hot climate and low humidity, without being smitten with the urge to build solar ponds. On my first arrival at the plant both solar and spray ponds were already under experiment, and I did not escape the contagion. As the work progressed, however, two things gradually became clear. First, as a method of separating the brine salts from each other solar evaporation whether in still or spray ponds is quite unreliable. The brine is completely saturated with five salts at 22.5° C. Evaporation near this tem-

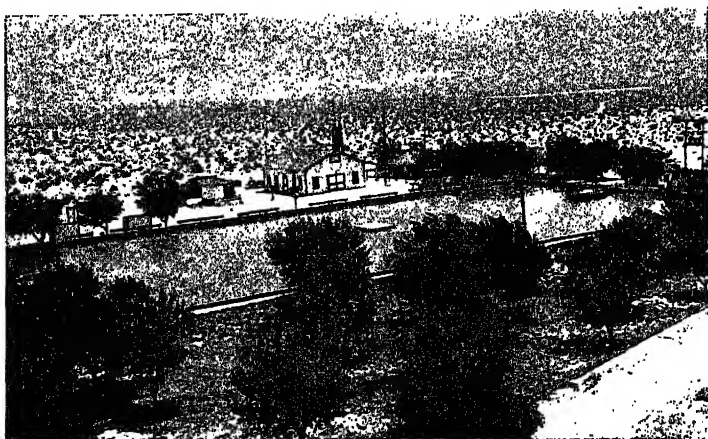


AIRPLANE VIEW OF TRONA PLANT AND PART OF VILLAGE.
Playa to right; lake upper right; slate range mountains beyond.

perature tends to precipitate most of them without producing much separation. Higher temperatures can not be maintained with good evaporation, and lower temperatures produce unlovely mixtures of highly hydrated carbonates, sulfates and borates, which are very difficult to handle. An operation might be developed but it would always be tricky and unreliable, and would require definite temperature control. Unfortunately the research department never produced a satisfactory method of controlling the weather.

If we abandoned the idea of making adequate and profitable separation of the salts by solar evaporation, there still remained the possibility of evaporating to dryness in solar ponds, and so reducing the cost of plant evaporation. At first sight this seems feasible. The sun is capable of evaporating, in one year at Trona, a layer of water about

9 feet deep. Brine having lower vapor pressure might show 5 feet water evaporation per year if the surface is kept free from crusts; a space the size of an 8 by 10 rug might suffice to precipitate 7 tons of salts per year, of which 1 ton would be KCl and 1200 pounds borax. To offset this pleasant prospect we must harvest this 7 tons of salts, transport it several miles to the plant, and hot leach or otherwise dissolve the valuable part, besides the care, maintenance and pumping at the pond, all to avoid evaporating 13 tons of water in the plant. In addition to this we would be faced with a relatively expensive raw material at the plant, whose cost could not be ignored. This would make percentage recovery an important item and would change the whole aspect of the problem.



VALLEY WELLS RESERVOIR CONTAINING WATER FOR PLANT USE. A SPACIOUS AND POPULAR SWIMMING POOL FOR ABOUT EIGHT MONTHS IN THE YEAR.

So long as triple-effect evaporation was expensive this alternative had to be examined with great care, but after plant evaporation was under control and could be done at a reasonable cost solar ponds no longer held any interest whatever, and the sun could shine at its own pleasure untrammelled by any extra cares in connection with the manufacture of potash or borax. The sun is not always the cheapest thing to use in a given operation merely because it furnishes B.t.u.'s for nothing.

We are accustomed to thinking of chemical plants in the center of civilization with immediate access to all requirements. One particular feature about Trona to be noted is its isolation. A plant located in such a place must be entirely self-sufficient. It must maintain in its stores not only everything that might be needed for repair and maintenance and operation of the plant, but absolutely everything that a community of

a thousand people may need for its physical, mental or spiritual welfare, whether the need is for a hundred-horsepower motor or a package of safety pins, a head of fresh lettuce or an evening at the movies. The corporation must have it in stock or else it is unobtainable anywhere. The corporation owns the plant, the town, the streets, the roads, the railroad, the schoolhouse, all the residences, the store and movie palace, swimming pool, water works, electric light and power, ice plant, the hospital, jail, and fire department. It is as nearly a complete soviet as I have ever seen, understanding "soviet" to mean the rule of a powerful minority. There are only two places in the city of Trona where anyone excepting an employee and his family or a guest may be without being guilty of trespass; those two places are the post office, where he may linger so long as he is buying a stamp or mailing a letter, and the waiting room of the railroad station, where he may wait for the next train. This concentration of authority in the hands of a few is rather necessary if one is to develop a project of this size in such an isolated region, and it requires a special kind of experience to guide such a community wisely. When I first saw the place in 1919 it had the same concentration of authority that it has to-day, but at that time it had more the aspect of a mining camp. Fortunately, the first manager we sent out, H. S. Emlaw, was a mining engineer who had had very considerable experience in handling isolated mining camps. To-day there are a number of men at the plant who could handle such a situation intelligently, but at that time it was a new experience to all the rest of us. In the early days of this enterprise the mining camp atmosphere was a necessity, and among men in subordinate positions a strong jaw, a good right arm and a powerful voice were probably more important qualifications than a knowledge of chemistry. If the enterprise were to really reach mature development, however, it was necessary to change the mining camp atmosphere and gradually develop a city with a large chemical works. A strong jaw and a good right arm are still valuable assets, as they are anywhere where things are to be done, but foremen and superintendents of the type that were once useful and necessary would be entirely lost in any attempt to understand the technical control which the present plant requires of their successors.

In the early stages of the work when it still bore the aspects of a mining camp it suffered from the same labor difficulties that such a camp expects. Large numbers of men employed were drifters who expected to work only a few weeks and then move on. At one time the labor turnover of the whole plant was at the rate of 500 per cent per year; on an average each workman stayed ten weeks. Such a situation would be

impossible in a well-controlled chemical plant where experience in the job is an important asset. Now that there is an attractive village and good surroundings there is no serious difficulty in keeping good workmen, and the labor turnover is only normal.

In the early days of my connection with this industry I found a very widespread disbelief in the possibility of its success. This was no doubt assiduously fostered by those who feared that it might be a success. I dislike the use of the word propaganda, but nothing else seems to describe suitably the great flood of articles, interviews and statements appearing regularly in newspapers, magazines, and even our technical journals, all of the same general tenor. The burden of their song was that God had given potash to Germany. He had given it in great quantities and easily accessible, and it was a crime, not much short of sacrilege, to try to manufacture it in the United States. There could be no hope of successful issue from such an attempt in times of peace. We could not possibly manufacture it as cheaply as Germany could, our source was a long freight haul from any market, and in any case our potash was not any good because it contained borax which would destroy the crops. We were, of course, also attempting to compete on borax, and our borax friends added their contribution to the effect that we could never make a really good borax, which was a matter of great care and intuition and of knowledge that could only be acquired over many years of experience. We might make something for a little while, but as soon as our philanthropists quit advancing money to us the thing would all be over. I even found a great many of my own acquaintances divided in opinion into two groups, one of which assumed that I was fooling myself, and the other, more charitably, decided that I was only fooling my clients. This current of thought, which was maintained for a good many years, and which I have not overdrawn, made it rather difficult for me to induce high-grade men such as I wanted to take a part in the enterprise. They feared to be damaging their own future by wasting time on an affair that was doomed to failure. However, there are always adventurous spirits, and not all my friends believed either that I was fooling myself or that I was fooling my clients, so we were able finally to staff the plant with high-grade technically trained men.

In a producing plant of this kind it is of course necessary that the research and development departments should be composed largely of men who are chemists or chemical engineers, and that a considerable proportion of the operating department should have that training also. The important thing, however, to my mind is technical training, not

necessarily chemical training. The first manager we sent out to the plant in 1919, Mr. Emlaw, was a mining engineer. His successor, Mr. Vieweg, who had been there as assistant manager, is a civil engineer. The present assistant manager, Mr. Mumford, formerly head of research and development, is a chemical engineer. The second assistant manager, Mr. Burke, also formerly head of research and development, is a chemist. The present head of research and development, Mr. MacDonald, is a chemical engineer. The present production manager, Mr. de Ropp, is a chemist. The head of the engineering department, Mr. Eason, is naturally a mechanical engineer. The head of the sales department, Mr. Holmes, is a mechanical engineer. Probably I do not make the same distinction between chemical engineers and chemists that is commonly made. From both one demands a certain knowledge of chemistry and a certain ability in the technic of handling materials. The distinction lies largely in the amount of material they need to have in hand in order to be at their very best level of thought. Both are engaged in the chemical transformation of matter, but a good chemical engineer thinks best and works best when he is dealing with tons. He can visualize and arrange his equipment better, his manipulations go more smoothly, his whole manner of thought is freer and clearer if he pictures a regular succession of tons of material flowing through an operation. A man well-adapted to development work, however, probably thinks best in pounds or hundreds of pounds. A chemist thinks best and works best in grams. You can convert a chemist into a chemical engineer by once getting him thoroughly interested in the idea of tonnages. If his mind is at all adapted to that quantity of matter his interest will be awakened and he will learn the technic of handling tons without a great deal of difficulty. On the other hand, it is not difficult to convert a chemical engineer into a chemist by interesting him in the quickness and accuracy with which he may obtain information from working only with grams instead of tons. If his mind is at all adapted to that quantity he will master the technic of handling grams. To my mind it is largely a question of the quantity of material the individual mind likes to consider at one time. To carry the comparison a little farther, I suppose we should say that a physical chemist is one who works best and thinks best with molecules rather than with grams or tons, probably not to exceed ten or a dozen molecules at one time, and the modern physicist is at his very best inside the spacious confines of a single atom.

No matter what kind of chemist or engineer a man may call himself he must have a training which enables him to understand the language

and something of the problems of chemistry and engineering, and he must habitually have a scientific and logical mode of thought.

It has been a matter of some surprise to many visitors to the plant, that trained and capable technical men such as they find there can be persuaded to stay in the desert away from civilization so many years and still be content. Of course they are only a few hours from civilization, or at least from Los Angeles and Hollywood; their living conditions are now very comfortable, society is congenial, work interesting, opportunity great, and business relations conducted on a basis of mutual respect. Why shouldn't they be content?

The matter of maintaining an atmosphere of mutual respect is of course advisable anywhere, but it becomes exceedingly important when dealing with technical men from whom you expect constructive work and ideas. My lecture to young men who are about to assume a position giving them some authority over other technical men runs about as follows:

(1) Don't strut; the fact that you now have a certain title or position is extremely unimportant to everyone but yourself. It doesn't prove anything. Maybe in selecting you someone made a mistake which will be rectified later. The essential thing is, what can you do, what can you contribute, how much better are you than a vacancy in the office? Crazy Ludwig was king of Bavaria, and Caligula's horse was consul of Rome. These were important events to Ludwig and maybe to the horse but they can hardly be counted as factors in successful progress.

(2) Never hesitate to make a decision. Never pass it up to your superiors unless it involves factors quite outside your province and beyond your control which might adversely affect other departments. Likewise insist on your subordinates making their own decisions whenever humanly possible. It may make you feel tremendously important to hold conferences and issue edicts, but it isn't good for the men, nor in the long run is it good for the business. Help them whenever you can, advise with them on matters where your judgment or experience may be better than theirs, see that they have the vision of what you are aiming at, but be very chary about issuing orders, and never place responsibility on a man without at the same time giving him adequate authority. Have a genuine respect for other men who are really doing anything, whether your subordinates, associates or superiors. Every one of them is probably a better and abler man than you are in some particular kind of work. See to it that there is some work that you do better than any of them in order to maintain their respect too. The

man who has not a real appreciation for the work of other men should be allowed to depart from an organization quietly and quickly.

(3) Don't overwork the push button, and don't be a fusser. When men are on the carpet in your office they are not doing the work for which they are paid, and weeks afterwards they may be resenting unfair things you said, instead of doing constructive work.

(4) Play fair; no alibis. If something goes wrong don't hesitate to take the blame. We can forgive honest mistakes when a man tries to do something. What we can't forgive is the mistake of the man who is afraid to do anything. If the thing happens to go just right then remember that you probably didn't accomplish it all alone and entirely unaided. Maybe there were others present. A position of responsibility means an opportunity for leadership. If you haven't the quality of leadership all the authority in the world will not confer it on you; it must be developed inside yourself.

This is rather a long lecture to interpolate here, but I probably never delivered it all at one time before, and it is part of the story. Furthermore at this time when business is so permeated with glorified office boys who call themselves executives it seems wise to call attention again to a few of these fundamentals.

After the plant had come through its early difficulties and had reached a fairly steady output, it became important to bring the production to as high a level as could consistently be done. In such work slight inattention on the part of the operators, or a little slowness on the part of maintenance men who are routed out of bed at 2 A.M. may mean a loss of hundreds or thousands of dollars. So it seemed wise to establish production bonuses in favor of certain foremen, operators, and maintenance men to spur them to special attention and speed. As a part of this program complete production figures were posted in the plant every day for the inspection of all concerned. There may be some doubt regarding the general advisability of making such payments, but I think none of the responsible men at the plant has any doubt that it was a very important factor in capturing the interest of a class of men who are often uninterested in anything except pay day, and in bringing production to a fairly high level.

For my own convenience I habitually cast operating figures into a per diem form because my mind visualizes better in thousands of dollars than it does in millions. During the early days of Trona operation the question was whether the existing plant could operate or should be scrapped, consequently depreciation, amortization, obsolescence, interest on investment and similar items had no place in the figures. Our interest

lay only in current income and outgo, so the average figures per day, made up once per month from the monthly totals, looked about as follows:

Average Daily Expenses

1. Operating labor
2. Fuel
3. Repair and maintenance
4. Electric power purchased
5. Supplies
6. Administration
7. Sundry plant and village expenses
8. Selling expense
9. Miscellaneous interest, insurance, taxes, etc.

Against this was offset the value of the product made each day. The figure used here was the average return per ton for the previous month, net, naked in the warehouse after deducting all freights, commissions, loading, handling and packaging charges.

— tons KCl per day at	—	—
— tons borax per day at	—	—

The difference between expense and approximate value of product per day gave a rough operating margin which could easily be followed from month to month. This statement is handed to all heads and sub-heads of departments every month and has been an important factor in maintaining a keen interest among the technical men, and particularly in developing their sense of the relative importance of things, the comparative efficiency of their own department and its relation to the whole operation. The statement has undergone repeated revision and expansion as the operation took on more of the aspect of a regular business, always keeping in mind that the responsible men should have an accurate knowledge of all money values involved. I don't like to see men working in the dark. It is particularly distressing to have research and development men struggling with problems that might at the most mean \$10 or \$20 per day, and calmly ignoring factors that may involve hundreds or thousands simply because they lack an accurate knowledge of proportional money values. Many firms are exceedingly secretive regarding all money figures. It may be a petty misdemeanor to allow your cost figures to reach a competitor, particularly if your costs are such that you ought to be ashamed of them, but it is a major folly to keep your own good men in ignorance of them. A still greater folly is not to know them yourself.

In developing a pioneering job of this kind where so little is surely known and so little is standardized, one should not be content until

a thorough personal interest has been aroused as far down the line as the degree of intelligence and the personal character of the individual will permit. In the present case the responsible men, especially in research, development, operation, engineering and sales feel, and feel rightly, that they have made the business. They can each look with the eye of a fond parent on some contribution in which they had a part, with the knowledge that without them it might not have been done so well, or possibly not at all. When men reach that stage they are no longer simply the occupants of positions and holders of jobs. Their pride is not in what *I am* but in what *I do*, which makes a tremendous difference in their real value in any walk in life.

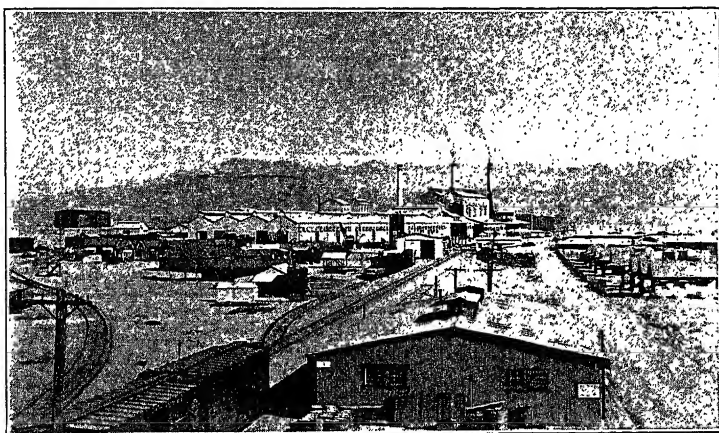
CHAPTER VI.

THE PRESENT PLANT.

By the middle of 1924 the plant was operating steadily, sales were going smoothly, income showed a regular margin above outgo, and everyone interested agreed that the time had come to center efforts on the design and construction of a real plant. Over a year was spent in gathering further information, largely from large-scale development work; then construction began with as little interruption of operations as possible (which is always bad enough). The first unit was started in October, 1926, and the second one early in 1927. In the design it was expected that when the new plant was properly tuned up it should have a capacity of about 125 tons borax and 250 or more tons KCl per day, all in marketable form, a part of the borax being afterward converted into boric acid. Like all new plants it went through several months of tuning up, adjusting, training men to its use, and allowing the operating heads to determine its usual habits, and the points toward which particular attention should be directed. This was finally accomplished, nothing of importance was found to be fundamentally wrong in design, and its present performance is just slightly in excess of the prospectus. When I made my first guess at the total plant cost in 1924 many parts of the proposition were still rather vague, consequently the guess was none too good; but we finally have a better plant than I had first visualized, and the per ton cost of production is enough lower than the original guess to more than compensate for added plant cost.

The problem as I saw it was, first, one of tonnage and fairly large units. There is no use in fooling with an operation of this kind unless your daily income from marketable products is sufficient to warrant the time, money and efforts of good men being spent on it; and the units in which the plant operates must be as large as conveniently possible, because it takes very little more labor and attention to operate a large unit than it does a small one, if you know how it is going to operate. Secondly, the total tonnage of the two products was set at about 375 tons per day, which was determined to some extent by the size of the boiler plant, refrigeration capacity, buildings, evaporators,

etc., that were available, and it was determined to produce this amount in two units. The second fundamental seemed to be continuity of operation. Continuous equipment so far as possible, no delays for washing equipment, no material coming back for reworking excepting a certain amount of mother liquor through the regular channels provided for it, and no delays from accidents. The raw brine from the lake should flow in at one end of the plant and finished potash and borax flow out into the warehouse at the other end, as nearly as possible in one uniform stream. Any material in the plant, anywhere, was to be considered as having no value excepting the time, labor and fuel that had



VIEW OF PLANT AT TRONA LOOKING WEST OF NORTH.

actually been spent on it, and the burden of proof lay on that particular material if it went wrong to determine that it should not be discarded rather than try to get back into the system. With this view of raw material in mind there was no particular stress for high yields, and it was obvious that if we were to produce say 250 tons of KCl per day we must pump into the plant considerably more than that amount. Let us assume, for this is not the figure but it will do perfectly well for illustration, that we had determined to pump to the evaporators one ton of brine every ten seconds. This would be 8640 tons per day, with roughly the following composition:

NaCl	1420 tons
Na_2SO_4	590 "
Na_2CO_3	420 "
KCl	400 "
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	200 "
Na_2PO_4	14 "

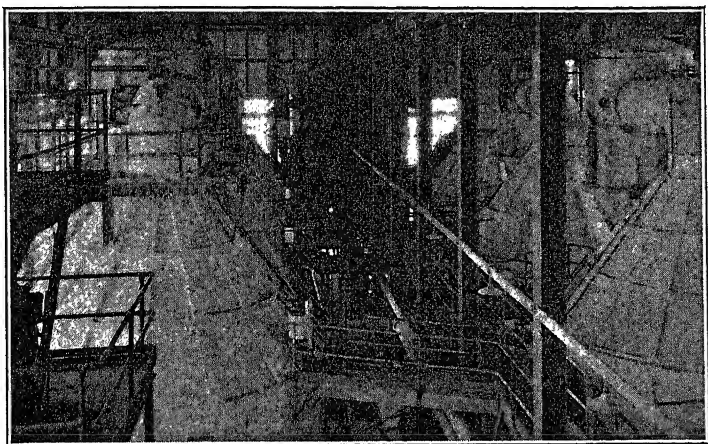
of which we only expected at the moment to recover and market about 375 tons. This would leave about 2600 tons of waste salts to be disposed of and 5600 tons of water per day to be evaporated in triple-effect evaporators, or lost. The boiler house uses fuel oil which is the only fuel accessible in this region, and has a rated capacity of 7000 hp. The steam produced goes directly to turbo-generators which furnish all the power and light required by both plant and village. Exhaust from the turbines goes to the first effects of triple-effect evaporators.

I do not consider it a part of the duty of the chemical engineer to design boilers, steam turbines, generators, or other electrical equipment. These things are standardized, and he has done his whole duty if he has seen that the right ones are selected and that they are functioning properly; but when it comes to a question of evaporation the chemical engineer must step in. The problem is different with every new material that he undertakes to concentrate. In a few lines, such as evaporation of water and of sugar solutions, practice has almost reached the stage of standard equipment, but in such a problem as the one we have before us the chemical engineer must determine what he wants to accomplish, collect the necessary data, and probably design a good part of the equipment. In our case we had a relatively narrow field within which concentrations and temperatures might be varied. A proper mixture of raw brine and mother liquors was to be fed to the third effect. If this liquor becomes too concentrated for the temperature of the third effect, potash as glaserite, and probably borax, will be precipitated and lost in the waste salts; or looked at in another way, if the temperature of the third effect is too low for the concentration of the liquors the same thing will happen. We have an identical problem in the second and first effects. We must decide either on the concentrations or on the temperatures to be reached in the different effects before the design of the apparatus can begin.

Now, a triple-effect evaporator consists essentially of three pans and each pan is composed of a heater, a flashing chamber, and the vapor lines. It is quite common practice to have the heater an intimate part of the flashing chamber and to have the heating area in the three pans more or less uniform. There is no particular reason for either, excepting the beautiful symmetry of the finished apparatus. In our case it was essential that the heater should be accessible for washing out salt deposits at frequent intervals without stopping evaporation. The obvious way to accomplish this was to have several different units of heaters connected with each flash chamber in such a way that any single heating unit could be cut off, washed and reconnected while the other heaters

were in full operation. This makes the operation of the evaporators as a whole continuous.

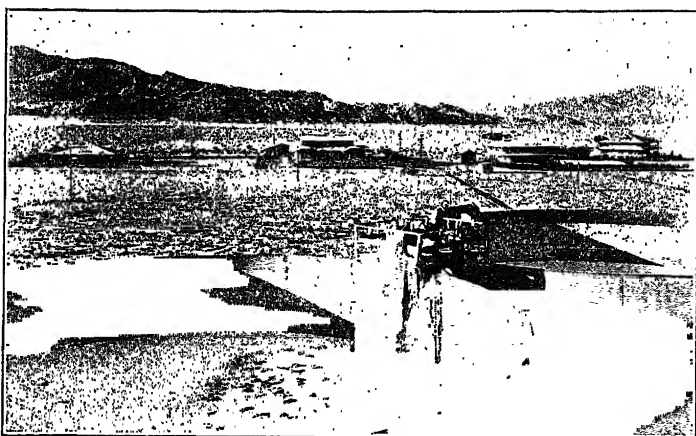
The amount of evaporation in each pan will be directly proportional to the temperature differential in that pan, between the condensing steam and the hot liquor, directly proportional to the heating area, and will vary, but not proportionally, with the speed of flow of the liquor. The first problem was to determine on a fair-size scale what flow of liquor through the heating tubes was most economical considering the cost of circulating the liquor, the coefficient of heat transmission through the tubes, the curve with which this transmission dropped, and the length



EVAPORATORS—TOP VIEW, SHOWING VAPOR LINES AND FOAM SEPARATORS.

of time the heater could be kept in operation without stopping to wash out. We found, as was to be expected, that for any given rate of flow the heat transmitted per square foot was far lower in the third or coolest effect than it was in the second effect, and the second in turn was lower than it was in the first. If we were given, then, equal heating surface in all three pans, and equal rate of flow, the evaporator would so adjust itself that our available temperature drop would be very largely taken up by the third effect. The second effect would have a smaller proportion, and the first effect the smallest. If one desired a uniform temperature drop in all three pans, which would seem to be the ideal toward which one should work, then the third effect should have the largest heating surface or the highest speed of flow, the second should be intermediate, and the first should have the lowest. Whether one gives the third effect the large heating area, or gives it the high speed,

becomes purely an economic question of plant cost *versus* operating cost, and naturally the whole design of the evaporators in relation to the heating area in each pan and the rate of flow in each pan will be decided on the same basis. Evaporating engineers seem to have reached the conclusion that something like six feet per second is a proper rate of flow, but I cannot see any basis for assuming that there is a proper rate of flow that is uniformly applicable. In some cases and in some pans the proper rate may not be over two feet per second, in other cases it may be as high as eight. In each case it becomes a question simply of weighing relative costs. Nine times out of ten it

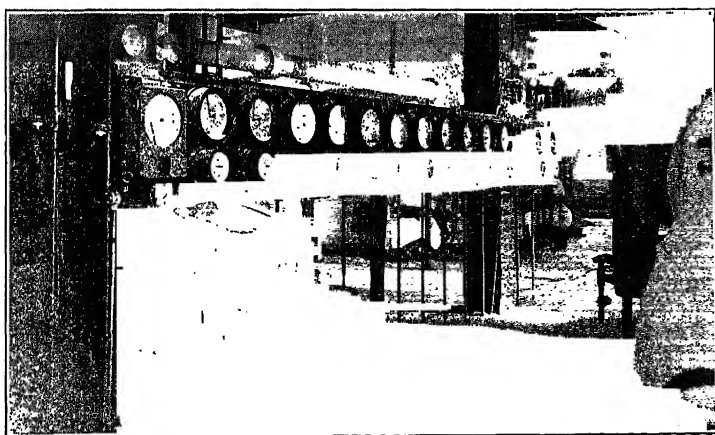


LOOKING WEST FROM TOP OF BRINE TANKS NEAR NORTHWEST CORNER OF THE PLANT.

will be found that a uniform heating area and uniform speed in all pans is economically unsound. Whether a uniform temperature drop in all pans is a proper ideal toward which to work I am not sure, but it is not far from the correct one. In our case, of course, we had to compromise with this ideal in order to meet the limitations of concentration and temperature in the different pans, and this will frequently be the case in such problems.

The equipment for evaporation as finally erected does not look like anything I ever saw before, but it is effective. The design of a novel apparatus of this kind involves features that concern the chemist, the chemical engineer, the mechanical engineer, and the operating man, so it is not surprising to find that Mr. Burke and Mr. MacDonald of the research department, Mr. Mumford, the assistant manager, Mr. Eason and Mr. Jackson of the engineering department, Mr. de Ropp of the

operating department, and even Mr. Vieweg, the civil engineer manager, all at some time took a part in the development of the evaporators, and particularly of the heating system. As a matter of fact, in designing a changed equipment, when one finally casts his mind entirely loose from the tradition of customary shapes, sizes and relationships, and looks only on the immediate limitations and demands of the problem in front of him, the apparatus designs itself in its broad outlines. It remains then only for the specialist to determine what particular arrangement of detail will make it most convenient to operate, most durable, and least likely to call for the repair and maintenance gang.



RECORDING INSTRUMENTS FOR EVAPORATORS.

Arrangement of flash chambers, vapor lines, condensers, etc., presented no particularly interesting problems. The only vapor line liable to give trouble is the one going from the third effect to the condenser. A pound of steam at that reduced pressure has a tremendous volume, and if the vapor line is too small the friction losses may unduly raise the boiling temperature of the third pan. One-tenth of an inch difference in the vacuum on the third pan means over a degree in boiling temperature. The steam may travel through this vapor line to the condenser at a rate of over 100 miles an hour without causing serious difficulty, but if an attempt is made to send it through at 200 miles per hour the loss in vacuum is noticeable.

One of the most interesting problems in connection with the evaporators is the removal of waste salt without undue loss of concentrated or partly concentrated liquor. We have over 2000 tons of this salt per

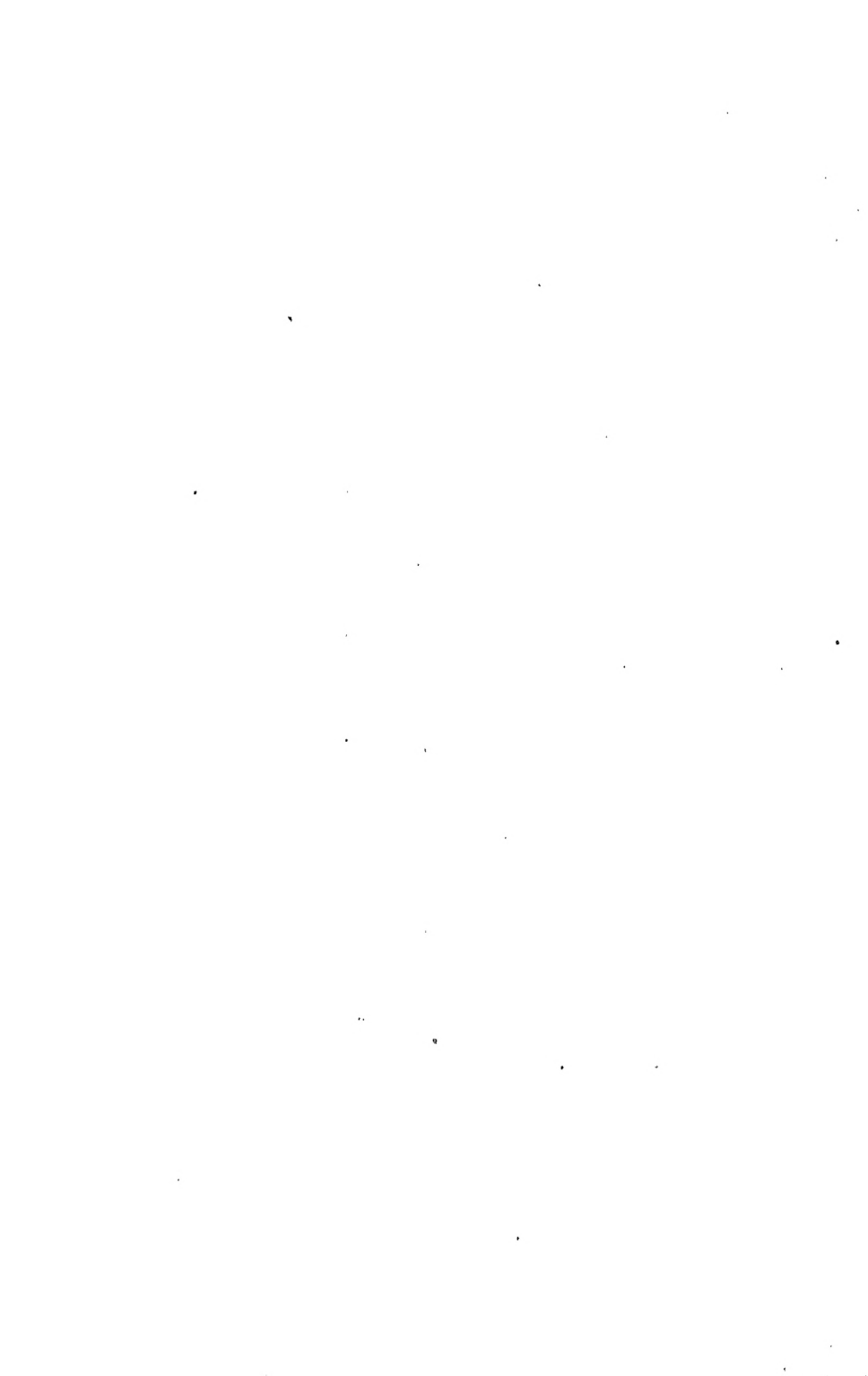
day, say at least 1 ton every 40 seconds, to be removed from the evaporators, separated from liquor, washed to remove partly concentrated liquor and discarded, and the liquor returned to the pans. This is all done in graded countercurrent washers and settlers designed largely by Francis MacDonald. This also is something that I never saw before, but it works. As a result of the evaporation we have some hundreds of thousands of gallons per day of hot concentrated liquor rich in potash and borax which must be cooled rapidly to crystallize the potash. Now the quickest way to cool a hot liquor is to subject it to a vacuum. Batch vacuum coolers are not new, but we thought for our purposes we must have a continuous apparatus, so it fell to Mr. Mumford to design continuous vacuum coolers. These proved very effective, and it is rather a surprise that they have not been more commonly designed for other purposes. After the liquor leaves the continuous vacuum cooler it passes through other continuous coolers which have been developed by Mr. Burke, then to settling tanks and centrifugals to remove the potash. From the time the liquor begins to cool until the potash has been washed in the centrifugals only a matter of minutes must be allowed to elapse, otherwise borax crystallizes also. This part of the plant is all arranged then for continuity and speed. When the potash leaves the centrifugals it passes through a drier and then to the warehouse. The liquor which is supersaturated with borax then passes to a continuous crystallizer, which is a weird looking object developed by Mr. Burke. Its purpose is to persuade the borax to crystallize in a form where it can be handled, and not in a disagreeable slime. It serves this purpose, and the borax is separated and refined while the mother liquor, still fairly rich in potash and borax, is returned for reuse. Of course at some stage these liquors must receive a certain degree of acidification to convert metaborate into borax. Otherwise there will be high concentration of metaborate in the evaporating pans, and undue losses. As will be seen, the process from start to finish is a fairly simple one, but the manipulation necessary to maintain every part of it within the narrow limits necessary to success requires a rather high degree of technology and of alertness.

I have not attempted to give any complete picture or any detailed description of the apparatus. What strikes the chemical engineer most on visiting the plant is probably its unconventionality so far as the appearance and use of apparatus is concerned, and the present plant being only the first attempt at this unconventionality will doubtless be greatly improved on the next attempt by the experience gained from this present one.

In the near future when the equipment has been partly superseded it may be possible to give details. Any chemical manufacturer should feel able to hand his dearest competitor all data, information and plans over five years old and still beat him. Mind, I do not say the information should be regularly handed to a competitor, but a chemical manufacturer should be so imbued with the spirit of progress, so alive to the future, so forward looking that he would feel able to do this, and in fact would be delighted to have his competitor doing to-day just what he was doing five years ago. If he doesn't feel that capability in himself I doubt whether he belongs in a field so subject to progress as the chemical business.

This is about all of the story to be told at present. The corporation is producing and marketing to-day between 20 per cent and 25 per cent of all the potash used in America, but its output would make no real impression on the amount that America ought to use. It is making and marketing nearly half the borax and a considerable per cent of the boric acid that the whole world uses, but borax has extremely valuable properties, and if it is kept where it belongs, in the class of cheap chemicals, the world will use to advantage several times its present consumption. There is plenty of room for expansion and it seems probable that most of the borax of the near future will come from sources like Searles Lake, rather than from colemanite and other borax minerals as it did ten or fifteen years ago.

Other materials in the lake are on the road to development, but their story can wait until it is history rather than prophecy.



PART II.

Equilibrium Data and Diagrams.

SYSTEM I*

Sodium Chloride, Sodium Sulfate, Sodium Carbonate, Water
(Diagrams 1, 2, 3, 4)

This is the first of the five four-component systems which must be examined in leading up to the five-component system, water and the chlorides, sulfates and carbonates of potassium and sodium.

Diagram 1 shows the chlorides, sulfates and carbonates of sodium plotted along the three rectangular axes in mols per thousand mols of water; the fourth component, water, being always 1000 mols, is not shown on the diagram. For convenience two data sheets are given at each temperature, one in grams per hundred grams of water, and the other in mols per thousand mols of water. The method of the data sheet is to show first the three two-component univariant points, 237, 238, 239, representing solubilities of the three single salts. Then the data are given for a three-component univariant point 241, followed by data for some point on the divariant line (between 237 and 241) representing equilibrium with $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, and some point on the divariant line (between 238 and 241) in equilibrium with $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. This gives the complete three-component system Na_2CO_3 , Na_2SO_4 and water at 20°C . Next data are given for the three-component univariant point 2, followed by two points on the divariant line between 237 and 2, then for point 243 and three points on the divariant line between 243 and 238, then point 1. We now have the three complete bounding three-component systems in the three planes, and it only remains to fill out the solid figure by giving data for the four four-component univariant points (246, 4, 249 and 3) at each of which solution is in equilibrium with three solid phases. The numerals designating univariant points may seem to jump about in an erratic manner, but they were

* Systems I to VI are by Harald de Ropp, with a very considerable amount of advice and assistance by William E. Burke. The hanksite portion of System VI is due to William E. Burke and W. A. Gale.

originally so numbered for convenient use and have not been changed for publication.

The field of the double salt burkeite is bounded by points 3, 4, 246, 249, and the lines connecting them. It will be noticed that no part of this field touches the plane of the three-component system Na_2CO_3 , Na_2SO_4 , H_2O . A temperature of 20°C . is below that at which burkeite can exist in equilibrium with solution of its two constituents alone, and at least 17.7 mols Na_2Cl_2 per 1000 mols water at point 246 are necessary for its stability. The same is true of course for anhydrous sodium sulfate.

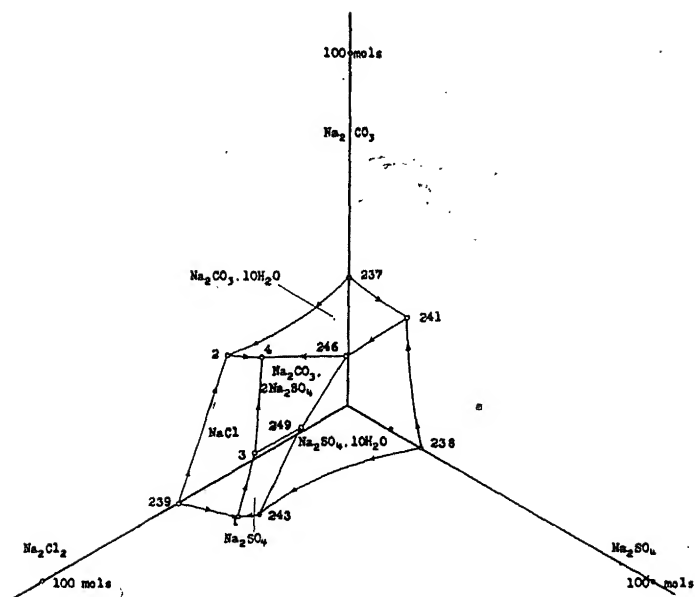
SYSTEM I— 20°C .
(Diagram 1)

Point	Solid Phases	Grams per 100 Grams of Water			
		Na_2CO_3	Na_2SO_4	NaCl	Total
237	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	21.5	21.5
238	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	19.5	...	19.5
239	NaCl	36.0	36.0
241	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	20.1	14.9	...	35.0
...	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	20.3	12.5	...	32.8
...	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	6.9	15.8	...	22.7
2	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, NaCl	19.8	...	25.4	45.2
...	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	18.0	...	9.9	27.9
...	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	17.4	...	17.2	34.6
243	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, Na_2SO_4	13.0	29.0	42.0
...	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	12.5	11.8	24.3
...	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	11.7	20.4	32.1
...	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	12.1	26.2	38.3
1	Na_2SO_4 , NaCl	11.0	31.8	42.8
...	NaCl	13.5	...	28.9	42.4
246	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, burkeite	18.8	13.8	11.5	44.1
...	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, burkeite	19.7	11.2	17.3	48.2
...	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	19.2	13.8	7.2	40.2
4	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, NaCl , burkeite	21.1	6.2	23.2	50.5
249	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, burkeite, Na_2SO_4	11.0	14.1	21.4	46.5
3	Na_2SO_4 , NaCl , burkeite	8.3	10.5	28.5	47.3

SYSTEM I— 20°C .
(Diagram 1)

Point	Solid Phases	Mols per 1,000 Mols of Water			
		Na_2CO_3	Na_2SO_4	Na_2Cl_2	Total
237	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	36.5	36.5
238	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	24.7	...	24.7
239	NaCl	55.5	55.5
241	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	34.2	18.9	...	53.1
...	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	34.5	15.8	...	50.3
...	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	11.7	20.0	...	31.7
2	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, NaCl	33.6	...	39.1	72.7
...	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	30.6	...	15.3	45.9
...	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	29.6	...	26.5	56.1
243	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, Na_2SO_4	16.5	44.7	61.2
...	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	15.8	18.2	34.0
...	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	14.8	31.4	46.2
...	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	15.3	40.4	55.7
1	Na_2SO_4 , NaCl	13.9	49.0	62.9
...	NaCl	22.9	...	44.5	67.4
246	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, burkeite	32.0	17.5	17.7	67.2
...	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, burkeite	33.5	14.2	26.7	74.4
...	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	32.6	17.5	11.1	61.2
4	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, NaCl , burkeite	35.8	7.8	35.7	79.3
249	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, burkeite, Na_2SO_4	18.7	17.9	33.0	69.6
3	Na_2SO_4 , NaCl , burkeite	14.1	13.3	43.9	71.3

SYSTEM 1; $\text{NaCl} - \text{Na}_2\text{SO}_4 - \text{Na}_2\text{CO}_3 - \text{H}_2\text{O}$; 20°C .



m - Burkeite Crystallisation Starting Point

4 - End Point of Crystallisation

DIAGRAM 1.

Diagram 2 represents the same system at 35° C. The dekahydrates of both Na_2SO_4 and Na_2CO_3 have disappeared and the burkeite field is greatly enlarged. The double salt is now in equilibrium with solutions of its constituents. A solution represented by any point on the line between 10 and 11 will precipitate burkeite on the addition of either carbonate or sulfate.

SYSTEM I—35° C.
(Diagram 2)

Point	Solid Phases	Grams per 100 Grams of Water				Mols per 1,000 Mols of Water			
		Na_2CO_3	NaCl	Na_2SO_4	Total	Na_2CO_3	Na_2Cl_2	Na_2SO_4	Total
5	Na_2SO_4	50.7	50.7	64.2	64.2
6	NaCl	36.3	...	36.3	...	55.8	...	55.8
7	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	48.8	48.8	82.9	82.9
8	$\text{NaCl}, \text{Na}_2\text{SO}_4$	33.6	9.2	42.8	...	51.8	11.7	63.5
9	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}, \text{NaCl}$	24.8	23.9	...	48.7	42.1	36.8	...	78.9
10	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}, \text{burkeite}$	45.8	...	6.9	52.7	77.8	...	8.7	86.5
11	$\text{Na}_2\text{SO}_4, \text{burkeite}$	18.5	...	34.3	52.8	31.3	...	43.5	74.8
12	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}, \text{NaCl}, \text{burkeite}$	24.2	23.2	2.7	50.1	41.1	35.7	3.4	80.2
13	$\text{Na}_2\text{SO}_4, \text{NaCl}, \text{burkeite}$	4.6	30.7	8.8	44.1	7.8	47.2	11.2	66.2

Diagrams 3 and 4 show the system at 50° C. and at 75° C., and an additional data sheet gives figures for a few points at 100° C. Concentration of any solution of NaCl, Na₂SO₄ and Na₂CO₃ at 75° will bring us (Diagram 4) either to Point 30 with very little Na₂SO₄ or to Point 31 with very little Na₂CO₃, depending on the initial proportions of these two.

System I - NaCl - Na₂SO₄ - Na₂CO₃ - H₂O - 50° C.

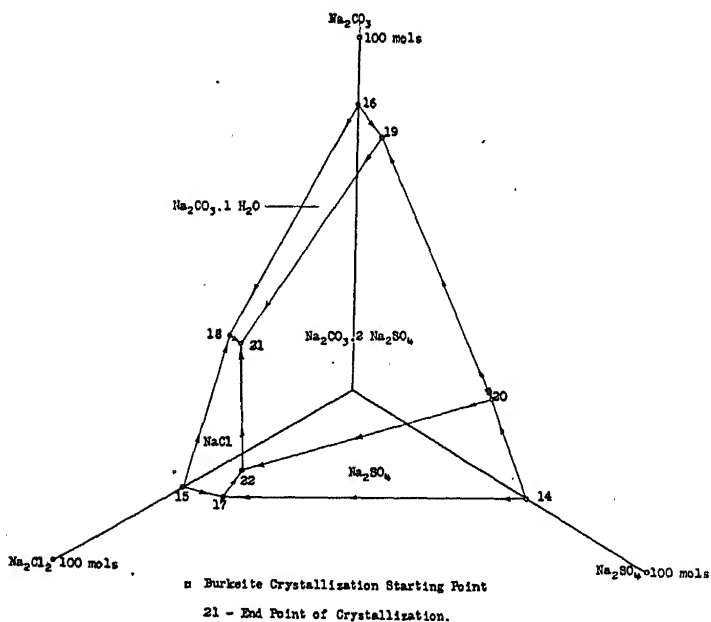


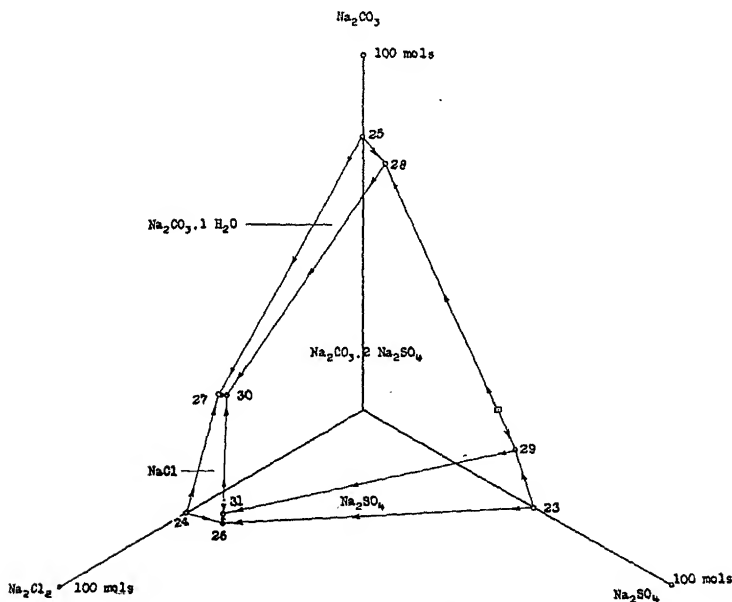
DIAGRAM 3.

SYSTEM I—50° C.
(Diagram 3)

Point	Solid Phases	Grams per 100 Grams of Water				Mols per 1,000 Mols of Water			
		Na ₂ CO ₃	NaCl	Na ₂ SO ₄	Total	Na ₂ CO ₃	Na ₂ Cl ₂	Na ₂ SO ₄	Total
14	Na ₂ SO ₄	46.6	46.6	59.1	59.1
15	NaCl	36.5	...	36.5	...	56.2	...	56.2
16	Na ₂ CO ₃ · 1 H ₂ O	47.5	47.5	80.6	80.6
17	Na ₂ SO ₄ , NaCl	33.7	7.3	41.0	...	51.9	9.3	61.2
18	Na ₂ CO ₃ · 1 H ₂ O, NaCl	20.9	27.0	...	47.9	35.5	41.5	...	77.0
19	Na ₂ CO ₃ · 1 H ₂ O, burkeite	44.4	...	6.3	50.7	75.4	...	8.0	83.4
20	Na ₂ CO ₃ · 1 H ₂ O, burkeite	12.6	...	36.7	49.3	21.4	...	46.5	67.9
21	Na ₂ CO ₃ · 1 H ₂ O, burkeite	20.2	26.4	2.0	48.6	34.4	40.6	2.6	77.6
22	Na ₂ CO ₃ · 1 H ₂ O, NaCl, burkeite	2.9	32.9	7.7	43.5	4.9	50.7	9.7	65.3

The transition point for $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ is very near 35°C ., and it possibly should occur in some of the 35° diagrams, but its field would be very small, and so it has been ignored.

System I - NaCl - Na_2SO_4 - Na_2CO_3 - H_2O - 75°C .



w Burkeite Crystallization Starting Point.

30 and 31 - End Points of Crystallization.

DIAGRAM 4.

SYSTEM I— 75°C .
(Diagram 4)

Point	Solid Phases	Grams per 100 Grams of Water				Mols per 1,000 Mols of Water			
		Na_2CO_3	NaCl	Na_2SO_4	Total	Na_2CO_3	Na_2Cl_2	Na_2SO_4	Total
23	Na_2SO_4	43.9	43.9	55.6	55.6
24	NaCl	37.8	...	37.8	...	58.2	...	58.2
25	$\text{Na}_2\text{CO}_3 \cdot 1\text{H}_2\text{O}$	45.3	45.3	77.0	77.0
26	NaCl - Na_2SO_4	35.5	6.8	42.3	...	54.7	8.6	63.3
27	$\text{Na}_2\text{CO}_3 \cdot 1\text{H}_2\text{O}$, NaCl	16.4	30.8	...	47.2	27.9	47.4	...	75.3
28	$\text{Na}_2\text{CO}_3 \cdot 1\text{H}_2\text{O}$, burkeite	42.9	...	5.4	48.3	72.8	...	6.8	79.6
29	Na_2SO_4 , burkeite	7.9	...	39.0	46.9	13.4	...	49.4	62.8
30	burkeite	16.6	30.3	1.4	48.3	28.1	46.7	1.8	76.6
31	burkeite	1.5	35.2	6.7	43.4	2.6	54.3	8.5	65.3

SYSTEM I—100° C.

Point	Solid Phases	Grams per 100 Grams of Water				Mols per 1,000 Mols of Water			
		NaCl	Na ₂ SO ₄	Na ₂ CO ₃	Total	Na ₂ Cl ₂	Na ₂ SO ₄	Na ₂ CO ₃	Total
32	NaCl, Na ₂ SO ₄	37.3	6.5	...	43.8	57.4	8.2	...	65.6
33	NaCl, Na ₂ CO ₃ .1H ₂ O	33.5	..	15.1	48.6	51.6	..	25.8	77.4
34	NaCl, Na ₂ SO ₄ , burkeite	37.2	6.7	1.2	45.1	57.2	8.4	2.0	67.6
35	NaCl, Na ₂ CO ₃ .1H ₂ O, burkeite	33.1	0.9	14.9	48.9	51.0	1.2	25.3	77.5

SYSTEM II

Potassium Chloride, Potassium Sulfate, Potassium Carbonate, Water
(Diagrams 5, 6, 7)

System II is a four-component system plotted on rectangular axes the same as System I and entirely comparable with that system except that it shows the potassium instead of the sodium salts. The most striking features of Diagrams 5, 6 and 7 are the absence of any double salt similar to burkeite, the enormous solubility of potassium carbonate, and the very slight solubility of potassium sulfate, especially in the presence of considerable amounts of the other two salts. A saturated solution of carbonate precipitates all but a trace of the sulfate, while neither chloride nor sulfate appreciably lowers the solubility of carbonate.

SYSTEM II—35° C.

(Diagram 5)

Point	Solid Phases	Grams per 100 Grams of Water				Mols per 1,000 Mols of Water			
		K ₂ CO ₃	KCl	K ₂ SO ₄	Total	K ₂ CO ₃	K ₂ Cl ₂	K ₂ SO ₄	Total
36	K ₂ SO ₄	14.1	14.1	14.5	14.5
37	KCl	39.0	...	39.0	...	47.1	...	47.1
38	K ₂ CO ₃ . $\frac{1}{2}$ H ₂ O	115.1	115.1	150.0	150.0
39	K ₂ SO ₄ , KCl	38.4	1.7	40.1	...	46.4	1.7	48.1
40	K ₂ CO ₃ . $\frac{1}{2}$ H ₂ O, KCl	114.1	3.1	...	117.2	148.7	3.7	...	152.4
41	K ₂ CO ₃ . $\frac{1}{2}$ H ₂ O, K ₂ SO ₄	112.5	...	Trace	112.5	146.5	...	Trace	146.5
42	K ₂ CO ₃ . $\frac{1}{2}$ H ₂ O, K ₂ SO ₄ , KCl...	112.7	2.9	Trace	115.6	146.8	3.5	Trace	150.3

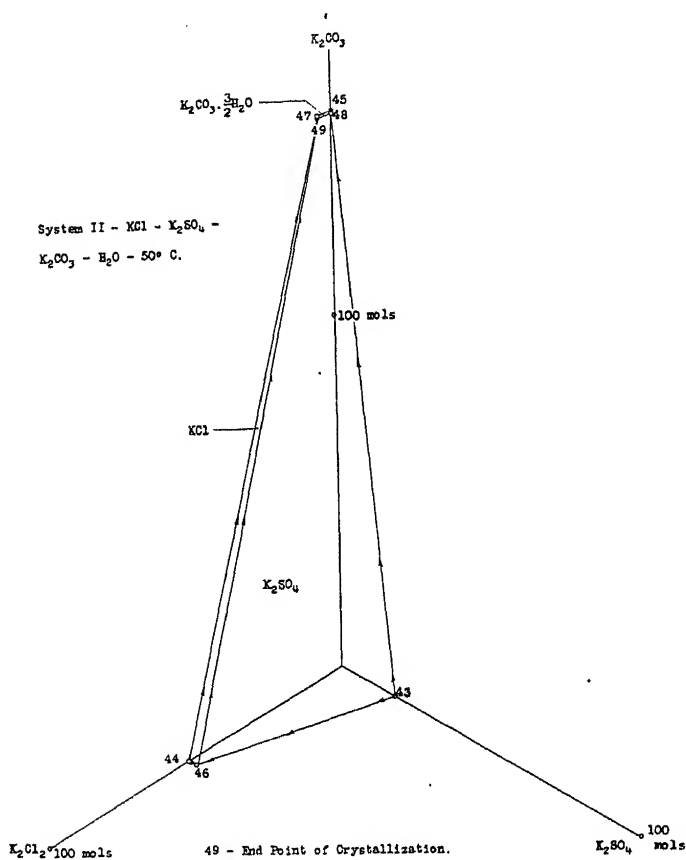


DIAGRAM 6.

SYSTEM II—50° C.

(Diagram 6)

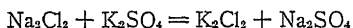
Point	Solid Phases	Grams per 100 Grams of Water				Mols per 1,000 Mols of Water			
		K ₂ CO ₃	KCl	K ₂ SO ₄	Total	K ₂ CO ₃	K ₂ Cl ₂	K ₂ SO ₄	Total
43	K ₂ SO ₄	17.1	17.1	17.6	17.6
44	KCl	43.1	...	43.1	52.1	...	52.1
45	K ₂ CO ₃ · 1/2 H ₂ O	121.2	121.2	157.9	157.9
46	KCl, K ₂ SO ₄	42.2	1.8	44.0	51.0	1.9	52.9
47	K ₂ CO ₃ · 1/2 H ₂ O, KCl	121.3	3.6	...	124.9	158.0	4.3
48	K ₂ CO ₃ · 1/2 H ₂ O, K ₂ SO ₄	121.2	...	Trace	121.2	157.9	...	Trace	...
49	K ₂ CO ₃ · 1/2 H ₂ O, K ₂ SO ₄ , KCl ..	121.2	3.6	Trace	124.8	157.8	4.3	Trace	...

SYSTEM III

Sodium Chloride, Potassium Chloride, Sodium Sulfate, Potassium Sulfate, Water

(Diagrams 8, 9, 10)

This is a four-component system because we have to do with reciprocal salt pairs:



and any set of analytical data for Na, K, Cl and SO_4 may be expressed in terms of not more than three of the salts. Point 65 in Diagram 8 may be expressed as 44.7 mols Na_2Cl_2 , 11.5 mols K_2Cl_2 , 13.3 mols Na_2SO_4 , being a net of 44.7 above and 1.8 to the left of the origin, or it may be expressed as 56.2 Na_2Cl_2 , 11.5 K_2SO_4 , and 1.8 Na_2SO_4 , reaching the same spot on the diagram. In either case point 65 is a point in space measured 69.5 mols on a perpendicular to the plane of the diagram, and what we have before us is the projection of a solid figure. This system as stated was investigated by Blasdale and our results do not differ materially from his excepting at points 66, 67 and 69 in Diagram 9, and points 72, 73 and 75 in Diagram 10, all at the boundaries of the glaserite field. While the two four-component systems previously examined each contained three three-component systems, this one, due to the reciprocal salt pairs, contains four three-component systems, one in each pair of axes. The most striking feature of the diagrams representing System III is probably the very large glaserite field. In addition to the three diagrams at 35°, 50° and 75° C., data sheets will be found for 20° and 100° C.

System III contains the important constituents of Searles Lake brine with the exception of carbonates and borax. The brine is saturated with NaCl and glaserite and nearly saturated with Na_2SO_4 . So far as the chlorides and sulfates are concerned we are very near the univariant point, connecting the three fields NaCl, Na_2SO_4 and glaserite at 22.5° C. An examination of the diagrams shows how impracticable it would be to make a separation of the salts or a concentration of KCl in the solution by evaporation at any temperature. We are continually losing large quantities of potash precipitated as glaserite along with sodium chloride. The presence of carbonate in the brine is what renders concentration by evaporation possible, and this is why methods that begin with a CO_2 treatment to remove carbonate are not commercially practicable if the next step is to be evaporation. Yet this is the first thought that comes to the minds of most chemists when given such a liquor for commercial treatment.

SYSTEM III—20° C.

Point	Solid Phases	Grams per 100 Grams of Water				
		NaCl	KCl	Na ₂ SO ₄	K ₂ SO ₄	Total
57	NaCl, KCl	29.9	14.8	44.7
1	NaCl, Na ₂ SO ₄	31.8	...	11.0	...	42.8
58	NaCl, KCl, glaserite	28.4	15.3	3.4	...	47.1
59	NaCl, Na ₂ SO ₄ , glaserite	28.2	7.6	12.1	...	47.9

SYSTEM III—20° C.

Point	Solid Phases	Mols per 1,000 Mols of Water				
		Na ₂ Cl ₂	K ₂ Cl ₂	Na ₂ SO ₄	K ₂ SO ₄	Total
57	NaCl, KCl	46.1	17.9	64.0
1	NaCl, Na ₂ SO ₄	49.0	...	13.9	...	62.9
58	NaCl, KCl, glaserite	43.7	18.4	4.3	...	66.4
59	NaCl, Na ₂ SO ₄ , glaserite	43.5	9.2	15.3	...	68.0

SYSTEM III—35° C.

(Diagram 8)

Point	Solid Phases	Grams per 100 Grams of Water				
		NaCl	KCl	Na ₂ SO ₄	K ₂ SO ₄	Total
5	Na ₂ SO ₄	50.7	...	50.7
36	K ₂ SO ₄	14.1	14.1
37	KCl	39.0	39.0
6	NaCl	36.3	36.3
60	Na ₂ SO ₄ , glaserite	48.8	7.9	56.7
61	K ₂ SO ₄ , glaserite	7.2	15.0	22.2
39	K ₂ SO ₄ , KCl	38.4	...	1.7	40.1
62	NaCl, KCl	29.8	18.4	48.2
8	NaCl, Na ₂ SO ₄	33.6	...	9.2	...	42.8
63	K ₂ SO ₄ , KCl, glaserite	8.1	32.0	2.6	...	42.7
64	NaCl, KCl, glaserite	27.8	19.1	3.6	...	50.5
65	NaCl, Na ₂ SO ₄ , glaserite	29.0	9.6	10.5	...	49.1

SYSTEM III—35° C.

(Diagram 8)

Point	Solid Phases	Mols per 1,000 Mols of Water				
		Na ₂ Cl ₂	K ₂ Cl ₂	Na ₂ SO ₄	K ₂ SO ₄	Total
5	Na ₂ SO ₄	64.2	...	64.2
36	K ₂ SO ₄	14.5	14.5
37	KCl	47.1	47.1
6	NaCl	55.8	55.8
60	Na ₂ SO ₄ , glaserite	61.8	8.2	70.0
61	K ₂ SO ₄ , glaserite	9.2	15.5	24.7
39	K ₂ SO ₄ , KCl	46.4	...	1.7	48.1
62	NaCl, KCl	45.9	22.2	68.1
8	NaCl, Na ₂ SO ₄	51.8	...	11.7	...	63.5
63	K ₂ SO ₄ , KCl, glaserite	12.4	38.6	3.3	...	54.3
64	NaCl, KCl, glaserite	42.8	23.1	4.5	...	70.4
65	NaCl, Na ₂ SO ₄ , glaserite	44.7	11.5	13.3	...	69.5

SYSTEM III—50° C.

(Diagram 9)

Point	Solid Phases	Grams per 100 Grams of Water				
		NaCl	KCl	Na ₂ SO ₄	K ₂ SO ₄	Total
14	Na ₂ SO ₄	46.6	...	46.6
43	K ₂ SO ₄	17.1	17.1
44	KCl	43.1	43.1
15	NaCl	36.5	36.5
66	Na ₂ SO ₄ , glaserite	47.4	9.3	56.7
67	K ₂ SO ₄ , glaserite	8.6	17.7	26.3
46	K ₂ SO ₄ , KCl	42.2	...	1.8	44.0
68	NaCl, KCl	29.1	22.0	51.1
17	NaCl, Na ₂ SO ₄	33.7	...	7.3	...	41.0
69	K ₂ SO ₄ , KCl, glaserite	8.7	36.4	2.3	...	47.4
70	NaCl, KCl, glaserite	26.8	22.4	3.1	...	52.3
71	NaCl, Na ₂ SO ₄ , glaserite	29.5	11.7	9.9	...	51.1

SYSTEM III—50° C.

(Diagram 9)

Point	Solid Phases	Mols per 1,000 Mols of Water				
		Na ₂ Cl ₂	K ₂ Cl ₂	Na ₂ SO ₄	K ₂ SO ₄	Total
14	Na ₂ SO ₄	59.1	...	59.1
43	K ₂ SO ₄	17.6	17.6
44	KCl	52.1	52.1
15	NaCl	56.2	56.2
66	Na ₂ SO ₄ , glaserite	60.1	9.6	69.7
67	K ₂ SO ₄ , glaserite	10.9	18.3	29.2
46	K ₂ SO ₄ , KCl	51.0	...	1.9	52.9
68	NaCl, KCl	44.8	26.6	71.4
17	NaCl, Na ₂ SO ₄	51.9	...	9.3	...	61.2
69	K ₂ SO ₄ , KCl, glaserite	13.4	43.9	2.9	...	60.2
70	NaCl, KCl, glaserite	41.4	27.0	4.0	...	72.4
71	NaCl, Na ₂ SO ₄ , glaserite	45.4	14.1	12.5	...	72.0

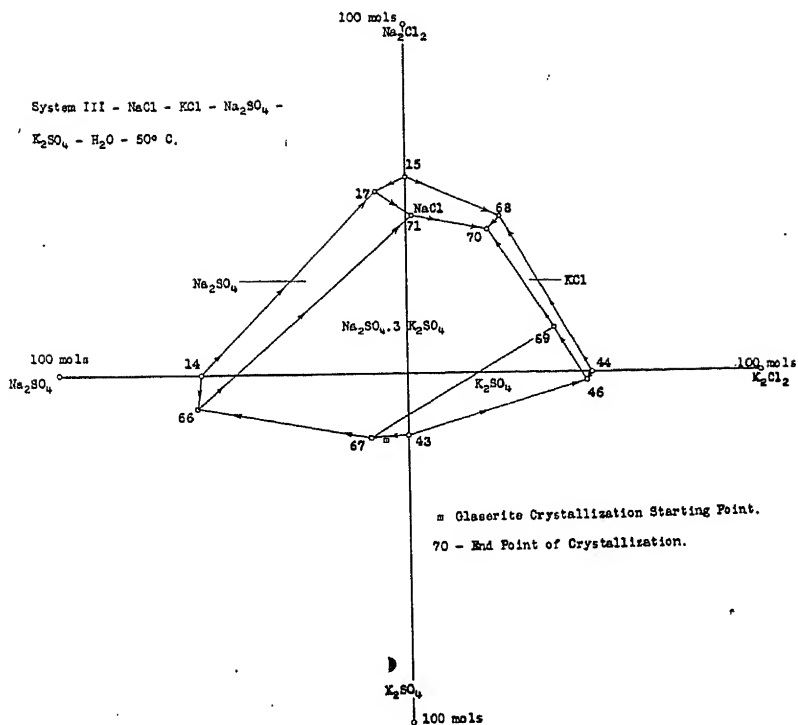


DIAGRAM 9.

SYSTEM III—75° C.

(Diagram 10)

Point	Solid Phases	Grams per 100 Grams of Water				
		NaCl	KCl	Na ₂ SO ₄	K ₂ SO ₄	Total
23	Na ₂ SO ₄	43.9	...	43.9
50	K ₂ SO ₄	20.6	20.6
51	KCl	49.7	49.7
24	NaCl	37.8	37.8
72	Na ₂ SO ₄ , glaserite	44.4	11.7	56.1
73	K ₂ SO ₄ , glaserite	8.1	21.8	29.9
53	K ₂ SO ₄ , KCl	48.5	...	1.9	50.4
74	NaCl, KCl	27.8	28.9	56.7
26	NaCl, Na ₂ SO ₄	35.5	...	6.8	...	42.3
75	K ₂ SO ₄ , KCl, glaserite	7.6	42.9	3.0	...	53.5
76	NaCl, KCl, glaserite	26.0	30.0	3.4	...	59.4
77	NaCl, Na ₂ SO ₄ , glaserite	28.5	16.0	8.8	...	53.3

SYSTEM III—75° C.

(Diagram 10)

Point	Solid Phases	Mols per 1,000 Mols of Water				
		Na ₂ Cl ₂	K ₂ Cl ₂	Na ₂ SO ₄	K ₂ SO ₄	Total
23	Na ₂ SO ₄	55.6	...	55.6
50	K ₂ SO ₄	21.3	21.3
51	KCl	60.0	60.0
24	NaCl	58.2	58.2
72	Na ₂ SO ₄ , glaserite	56.3	12.0	68.3
73	K ₂ SO ₄ , glaserite	10.3	22.6	32.9
53	K ₂ SO ₄ , KCl	58.5	...	2.0	60.5
74	NaCl, KCl	42.8	34.9	77.7
26	NaCl, Na ₂ SO ₄	54.7	...	8.6	...	63.3
75	K ₂ SO ₄ , KCl, glaserite	11.7	51.7	3.8	...	67.2
76	NaCl, KCl, glaserite	40.1	36.2	4.4	...	80.7
77	NaCl, Na ₂ SO ₄ , glaserite	43.8	19.3	11.1	...	74.2

SYSTEM III—100° C.

Point	Solid Phases	Grams per 100 Grams of Water				
		NaCl	KCl	Na ₂ SO ₄	K ₂ SO ₄	Total
78	NaCl, KCl	27.3	35.2	62.5
32	NaCl, Na ₂ SO ₄	37.3	...	6.5	...	43.8
79	NaCl, KCl, glaserite	25.2	36.3	3.7	...	65.2
80	NaCl, Na ₂ SO ₄ , glaserite	29.4	19.3	9.3	...	58.0

SYSTEM III—100° C.

Point	Solid Phases	Mols per 1,000 Mols of Water				
		Na ₂ Cl ₂	K ₂ Cl ₂	Na ₂ SO ₄	K ₂ SO ₄	Total
78	NaCl, KCl	42.0	42.5	84.5
32	NaCl, Na ₂ SO ₄	57.4	...	8.2	...	65.6
79	NaCl, KCl, glaserite	38.8	43.8	4.7	...	87.3
80	NaCl, Na ₂ SO ₄ , glaserite	45.3	23.3	11.7	...	80.3

SYSTEM IV

Sodium Chloride, Potassium Chloride, Sodium Carbonate, Potassium Carbonate, Water

(Diagrams 11, 12, 13)

System IV is another four-component system of reciprocal salt pairs, plotted like System III. Diagrams are given for 35°, 50° and 75° C., and data also for 20° and 100° C. One double salt appears, $\text{Na}_2\text{CO}_3 \cdot \text{K}_2\text{CO}_3$, apparently anhydrous at 35° and above. There are two end points of crystallization depending on the relative initial concentrations of K_2 and Cl_2 .

SYSTEM IV—20° C.

Point	Solid Phases	Grams per 100 Grams of Water				
		NaCl	KCl	Na_2CO_3	K_2CO_3	Total
57	NaCl, KCl	29.9	14.8	44.7
2	NaCl, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	25.4	...	19.8	...	45.2
81	NaCl, KCl, $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$	28.1	...	14.5	11.8	54.4

SYSTEM IV—20° C.

Point	Solid Phases	Mols per 1,000 Mols of Water				
		Na_2Cl_2	K_2Cl_2	Na_2CO_3	K_2CO_3	Total
57	NaCl, KCl	46.1	17.9	64.0
2	NaCl, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	39.1	...	33.5	...	72.6
81	NaCl, KCl, $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$	43.3	...	24.6	15.4	83.3

SYSTEM IV—35° C.

(Diagram 11)

Point	Solid Phases	Grams per 100 Grams of Water				
		Na ₂ CO ₃	K ₂ CO ₃	NaCl	KCl	Total
37	KCl	39.0	39.0
6	NaCl	36.3	...	36.3
62	NaCl, KCl	29.8	18.4	48.2
7	Na ₂ CO ₃ ·1H ₂ O	48.8	48.8
38	K ₂ CO ₃ ·½H ₂ O	115.1	115.1
40	K ₂ CO ₃ ·½H ₂ O, KCl	114.1	...	3.1	117.2
9	Na ₂ CO ₃ ·1H ₂ O, NaCl	24.8	...	23.9	...	48.7
82	Na ₂ CO ₃ ·1H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃	14.3	95.7	110.0
83	K ₂ CO ₃ ·½H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃	9.3	108.8	118.1
84	Na ₂ CO ₃ ·1H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃	23.1	...	16.8	16.9	56.8
85	Na ₂ CO ₃ ·1H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃ , KCl	12.0	97.2	2.5	...	111.7
86	K ₂ CO ₃ ·½H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃ , KCl	7.3	110.6	2.1	...	120.0

SYSTEM IV—35° C.

(Diagram 11)

Point	Solid Phases	Mols per 1,000 Mols of Water				
		Na ₂ CO ₃	K ₂ CO ₃	Na ₂ Cl ₂	K ₂ Cl ₂	Total
37	KCl	47.1	47.1
6	NaCl	55.8	...	55.8
62	NaCl, KCl	45.9	22.2	68.1
7	Na ₂ CO ₃ ·1H ₂ O	82.9	82.9
38	K ₂ CO ₃ ·½H ₂ O	150.0	150.0
40	K ₂ CO ₃ ·½H ₂ O, KCl	148.7	...	3.7	152.4
9	Na ₂ CO ₃ ·1H ₂ O, NaCl	42.1	...	36.8	...	78.9
82	Na ₂ CO ₃ ·1H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃	24.2	124.6	148.8
83	K ₂ CO ₃ ·½H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃	15.8	141.7	157.5
84	NaCl, KCl, Na ₂ CO ₃ ·1H ₂ O	39.2	...	25.9	20.4	85.5
85	Na ₂ CO ₃ ·1H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃ , KCl	20.3	126.6	3.8	...	150.7
86	K ₂ CO ₃ ·½H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃ , KCl	12.4	144.0	3.3	...	159.7

SYSTEM IV—50° C.

(Diagram 12)

Point	Solid Phases	Grams per 100 Grams of Water				
		Na ₂ CO ₃	K ₂ CO ₃	NaCl	KCl	Total
44	KCl	43.1	43.1
15	NaCl	36.5	...	36.5
68	NaCl, KCl	29.1	22.0	51.1
16	Na ₂ CO ₃ ·1H ₂ O	47.5	47.5
45	K ₂ CO ₃ · $\frac{1}{2}$ H ₂ O	121.2	121.2
47	K ₂ CO ₃ · $\frac{1}{2}$ H ₂ O, KCl	121.3	...	3.6	124.9
18	Na ₂ CO ₃ ·1H ₂ O, NaCl	20.9	...	27.0	...	47.9
87	Na ₂ CO ₃ ·1H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃	15.8	95.2	111.0
88	K ₂ CO ₃ · $\frac{1}{2}$ H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃	7.8	116.7	124.5
89	NaCl, KCl, Na ₂ CO ₃ ·1H ₂ O	19.4	...	18.6	20.8	58.8
90	Na ₂ CO ₃ ·1H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃ , KCl ...	12.5	97.0	3.6	...	113.1
91	K ₂ CO ₃ · $\frac{1}{2}$ H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃ , KCl	5.9	118.2	2.8	...	126.9

SYSTEM IV—50° C.

(Diagram 12)

Point	Solid Phases	Mols per 1,000 Mols of Water				
		Na ₂ CO ₃	K ₂ CO ₃	Na ₂ Cl ₂	K ₂ Cl ₂	Total
44	KCl	52.1	52.1
15	NaCl	56.2	...	56.2
68	NaCl, KCl	44.8	26.6	71.4
16	Na ₂ CO ₃ ·1H ₂ O	80.6	80.6
45	K ₂ CO ₃ · $\frac{1}{2}$ H ₂ O	157.9	157.9
47	K ₂ CO ₃ · $\frac{1}{2}$ H ₂ O, KCl	158.0	...	4.3	162.3
18	Na ₂ CO ₃ ·1H ₂ O, NaCl	35.5	...	41.5	...	77.0
87	Na ₂ CO ₃ ·1H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃	26.8	124.0	150.8
88	K ₂ CO ₃ · $\frac{1}{2}$ H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃	13.2	152.0	165.2
89	NaCl, KCl, Na ₂ CO ₃ ·1H ₂ O	32.9	...	28.6	25.2	86.7
90	Na ₂ CO ₃ ·1H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃ , KCl ...	21.2	126.4	5.6	...	153.2
91	K ₂ CO ₃ · $\frac{1}{2}$ H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃ , KCl	10.0	153.9	4.3	...	168.2

System IV - $\text{NaCl} - \text{KCl} - \text{Na}_2\text{CO}_3 - \text{K}_2\text{CO}_3 - \text{H}_2\text{O} - 50^\circ \text{C.}$

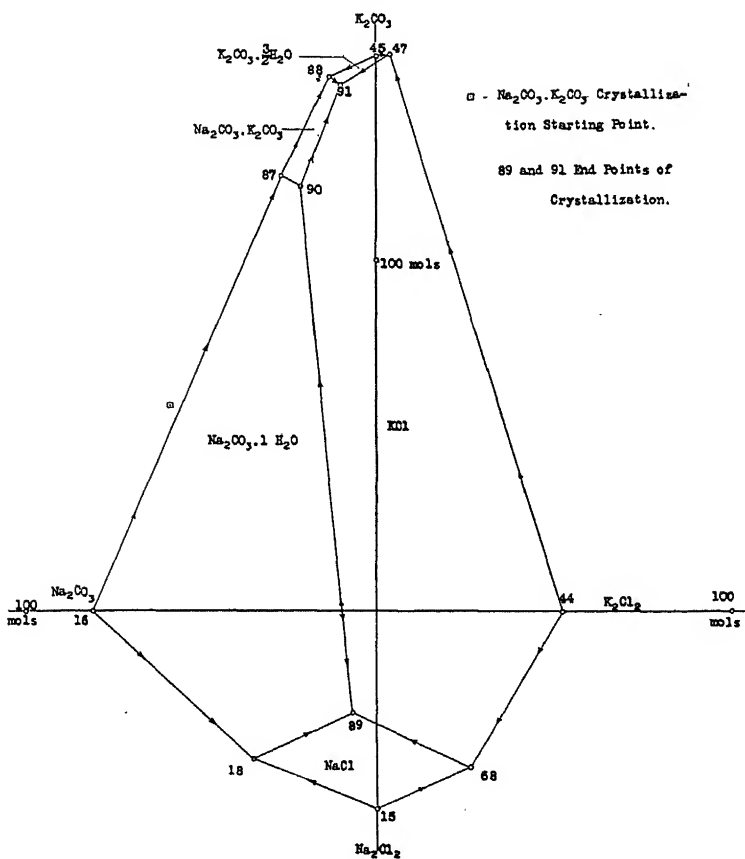


DIAGRAM 12.

SYSTEM IV—75° C.

(Diagram 13)

Point	Solid Phases	Grams per 100 Grams of Water				
		Na ₂ CO ₃	K ₂ CO ₃	NaCl	KCl	Total
51	KCl	49.7	49.7
24	NaCl	37.8	...	37.8
74	NaCl, KCl	27.8	28.9	56.7
25	Na ₂ CO ₃ ·1H ₂ O	45.3	45.3
52	K ₂ CO ₃ · $\frac{1}{2}$ H ₂ O	136.4	136.4
54	K ₂ CO ₃ · $\frac{1}{2}$ H ₂ O, KCl	134.9	...	5.2	140.1
27	Na ₂ CO ₃ ·1H ₂ O, NaCl	16.4	...	30.8	...	47.2
92	Na ₂ CO ₃ ·1H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃	18.0	94.2	112.2
93	K ₂ CO ₃ · $\frac{1}{2}$ H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃	5.1	133.5	138.6
94	NaCl, KCl, Na ₂ CO ₃ ·1H ₂ O	16.1	...	19.4	28.6	64.1
95	Na ₂ CO ₃ ·1H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃ , KCl	12.1	94.6	5.8	...	112.5
96	K ₂ CO ₃ · $\frac{1}{2}$ H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃ , KCl	0.6	138.7	3.8	...	143.1

SYSTEM IV—75° C.

(Diagram 13)

Point	Solid Phases	Mols per 1,000 Mols of Water				
		Na ₂ CO ₃	K ₂ CO ₃	Na ₂ Cl ₂	K ₂ Cl ₂	Total
51	KCl	60.0	60.0
24	NaCl	58.2	...	58.2
74	NaCl, KCl	42.8	34.9	77.7
25	Na ₂ CO ₃ ·1H ₂ O	77.0	77.0
52	K ₂ CO ₃ · $\frac{1}{2}$ H ₂ O	177.7	177.7
54	K ₂ CO ₃ · $\frac{1}{2}$ H ₂ O, KCl	175.7	...	6.3	182.0
27	Na ₂ CO ₃ ·1H ₂ O, NaCl	27.9	...	47.4	...	75.3
92	Na ₂ CO ₃ ·1H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃	30.6	122.6	153.2
93	K ₂ CO ₃ · $\frac{1}{2}$ H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃	8.6	173.9	182.5
94	NaCl, KCl	27.4	...	29.9	34.5	91.8
95	Na ₂ CO ₃ ·1H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃ , KCl	20.6	123.2	9.0	...	152.8
96	K ₂ CO ₃ · $\frac{1}{2}$ H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃ , KCl	0.9	180.6	5.8	...	187.3

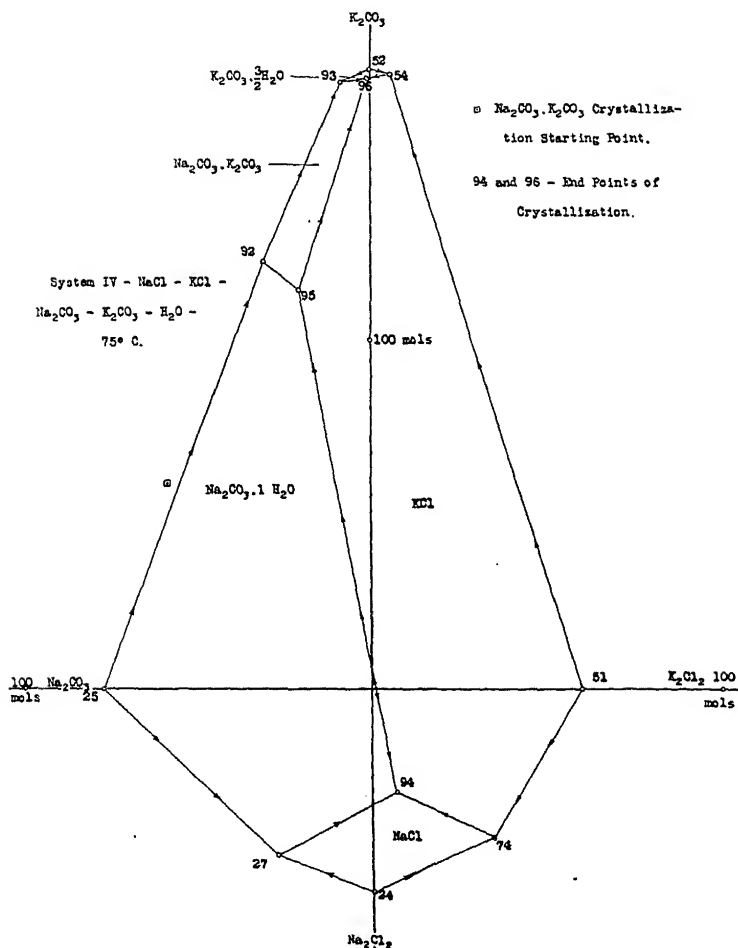


DIAGRAM 13.

SYSTEM IV—100° C.

Point	Solid Phases	Grams per 100 Grams of Water				
		NaCl	KCl	Na ₂ CO ₃	K ₂ CO ₃	Total
78	NaCl, KCl	27.3	35.2	62.5
33	NaCl, Na ₂ CO ₃ .1H ₂ O	33.5	...	15.2	...	48.7
97	NaCl, KCl, Na ₂ CO ₃ .1H ₂ O	35.2	15.2	...	18.0	68.4

SYSTEM IV—100° C.

Point	Solid Phases	Mols per 1,000 Mols of Water				
		Na ₂ Cl ₂	K ₂ Cl ₂	Na ₂ CO ₃	K ₂ CO ₃	Total
78	NaCl, KCl	42.0	42.5	84.5
33	NaCl, Na ₂ CO ₃ .1H ₂ O	51.6	...	25.8	...	77.4
97	NaCl, KCl, Na ₂ CO ₃ .1H ₂ O	54.2	18.4	...	23.5	96.1

SYSTEM V

Sodium Sulfate, Potassium Sulfate, Sodium Carbonate, Potassium Carbonate, Water

(Diagrams 14, 15, 16)

This is another four-component system with reciprocal salt pairs. In these diagrams we see for the first time the relation of glaserite and burkeite fields to each other, and the importance of an excess of sodium carbonate if we are to facilitate the precipitation of burkeite and keep the potash in solution. We also see that for a given excess of sodium carbonate a higher evaporating temperature enables us to stay longer in the burkeite field and reach a higher concentration of potash in solution. And finally we see something of the effect of solar evaporation. If in Diagram 14 we start with a solution of composition represented by point 100 and evaporate seven-eighths of the water we arrive at about point 102 by precipitating both burkeite and glaserite continuously. At this point about 85 per cent of the potash will be in a salt mixture in the ratio of about 1 mol potassium sulfate to 10 of sodium carbonate and sodium sulfate (just about the same proportion that we started with in the original solution) and the rest of the potash is in a solution which we have concentrated only from 7 mols to 10 mols K_2SO_4 per thousand of water. We would make no real progress toward concentration and separation that way.

SYSTEM V—35° C.

(Diagram 14)

Point	Solid Phases	Grams per 100 Grams of Water				
		Na ₂ CO ₃	K ₂ CO ₃	Na ₂ SO ₄	K ₂ SO ₄	Total
5	Na ₂ SO ₄	50.7	...	50.7
36	K ₂ SO ₄	14.1	14.1
7	Na ₂ CO ₃ ·1H ₂ O	48.8	48.8
38	K ₂ CO ₃ ·½H ₂ O	115.1	115.1
60	Na ₂ SO ₄ , glaserite	48.8	7.9	56.7
61	K ₂ SO ₄ , glaserite	7.2	15.0	22.2
82	Na ₂ CO ₃ ·1H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃	14.3	95.7	110.0
83	K ₂ CO ₃ ·½H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃	9.3	108.8	118.1
41	K ₂ CO ₃ ·½H ₂ O, K ₂ SO ₄	112.5	...	Trace	112.5
10	Na ₂ CO ₃ ·1H ₂ O, burkeite	45.8	...	6.9	...	52.7
11	Na ₂ SO ₄ , burkeite	18.5	...	34.3	...	52.8
98	Na ₂ CO ₃ ·1H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃ , K ₂ SO ₄ ..	14.1	96.1	Trace	...	110.2
99	K ₂ CO ₃ ·½H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃ , K ₂ SO ₄ ..	9.1	108.9	Trace	...	118.0
100	Na ₂ SO ₄ , burkeite, glaserite	17.0	...	31.8	6.9	55.7
101	Na ₂ CO ₃ ·1H ₂ O, K ₂ SO ₄ , glaserite	32.1	32.7	0.8	...	65.6
102	Na ₂ CO ₃ ·1H ₂ O, burkeite, glaserite	40.5	7.8	8.4	...	56.7

SYSTEM V—35° C.

(Diagram 14)

Point	Solid Phases	Mols per 1,000 Mols of Water				
		Na ₂ CO ₃	K ₂ CO ₃	Na ₂ SO ₄	K ₂ SO ₄	Total
5	Na ₂ SO ₄	64.2	...	64.2
36	K ₂ SO ₄	14.5	14.5
7	Na ₂ CO ₃ ·1H ₂ O	82.9	82.9
38	K ₂ CO ₃ ·½H ₂ O	150.0	150.0
60	Na ₂ SO ₄ , glaserite	61.8	8.2	70.0
61	K ₂ SO ₄ , glaserite	9.2	15.5	24.7
82	Na ₂ CO ₃ ·1H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃	24.2	124.6	148.8
83	K ₂ CO ₃ ·½H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃	15.8	141.7	157.5
41	K ₂ CO ₃ ·½H ₂ O, K ₂ SO ₄	146.5	...	Trace	146.5
10	Na ₂ CO ₃ ·1H ₂ O, burkeite	77.8	...	8.7	...	86.5
11	Na ₂ SO ₄ , burkeite	31.3	...	43.5	...	74.8
98	Na ₂ CO ₃ ·1H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃ , K ₂ SO ₄ ..	24.0	125.2	Trace	...	149.2
99	K ₂ CO ₃ ·½H ₂ O, Na ₂ CO ₃ ·K ₂ CO ₃ , K ₂ SO ₄ ..	15.4	141.8	Trace	...	157.2
100	Na ₂ SO ₄ , burkeite, glaserite	28.8	...	40.3	7.2	76.3
101	Na ₂ CO ₃ ·1H ₂ O, K ₂ SO ₄ , glaserite	54.5	42.6	1.0	...	98.1
102	Na ₂ CO ₃ ·1H ₂ O, burkeite, glaserite	68.8	10.1	10.7	...	89.6

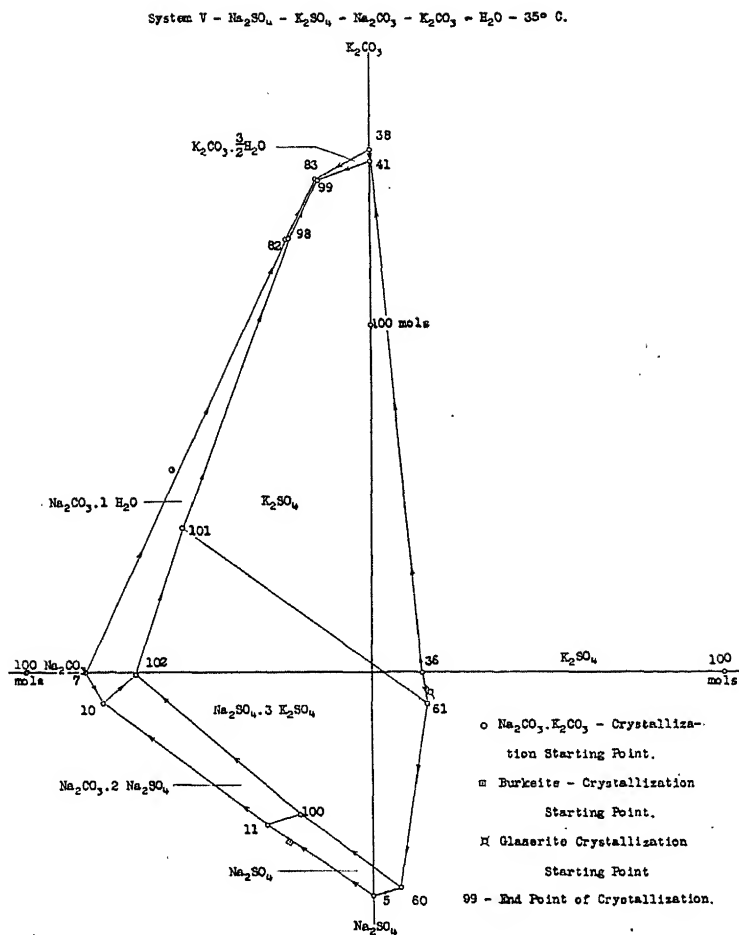


DIAGRAM 14.

SYSTEM V—50° C.

(Diagram 15)

Point	Solid Phases	Grams per 100 Grams of Water				
		Na ₂ CO ₃	K ₂ CO ₃	Na ₂ SO ₄	K ₂ SO ₄	Total
14	Na ₂ SO ₄	46.6	...	46.6
43	K ₂ SO ₄	17.1	17.1
16	Na ₂ CO ₃ ·1H ₂ O	47.5	47.5
45	K ₂ CO ₃ ·½H ₂ O	121.2	121.2
66	Na ₂ SO ₄ , glaserite	47.4	9.3	56.7
67	K ₂ SO ₄ , glaserite	8.6	17.7	26.3
87	Na ₂ CO ₃ ·1H ₂ O, Na ₂ CO ₃ , K ₂ CO ₃	15.8	95.2	111.0
88	K ₂ CO ₃ ·½H ₂ O, Na ₂ CO ₃ , K ₂ CO ₃	7.8	116.7	124.5
48	K ₂ CO ₃ ·½H ₂ O, K ₂ SO ₄	121.2	...	Trace	121.2
19	Na ₂ CO ₃ ·1H ₂ O, burkeite	44.4	...	6.3	...	50.7
20	Na ₂ SO ₄ , burkeite	12.6	...	36.7	...	49.3
103	Na ₂ CO ₃ ·1H ₂ O, Na ₂ CO ₃ , K ₂ CO ₃ , K ₂ SO ₄ ..	15.2	95.2	Trace	...	110.4
104	K ₂ CO ₃ ·½H ₂ O, Na ₂ CO ₃ , K ₂ CO ₃ , K ₂ SO ₄ ..	7.2	117.2	Trace	...	124.4
105	Na ₂ SO ₄ , burkeite, glaserite	6.8	6.9	43.1	...	56.8
106	Na ₂ CO ₃ ·1H ₂ O, K ₂ SO ₄ , glaserite	29.9	38.1	1.1	...	69.1
107	Na ₂ CO ₃ ·1H ₂ O, burkeite, glaserite	38.0	10.3	8.7	...	57.0

SYSTEM V—50° C.

(Diagram 15)

Point	Solid Phases	Mols per 1,000 Mols of Water				
		Na ₂ CO ₃	K ₂ CO ₃	Na ₂ SO ₄	K ₂ SO ₄	Total
14	Na ₂ SO ₄	59.1	...	59.1
43	K ₂ SO ₄	17.6	17.6
16	Na ₂ CO ₃ ·1H ₂ O	80.6	80.6
45	K ₂ CO ₃ ·½H ₂ O	157.9	157.9
66	Na ₂ SO ₄ , glaserite	60.1	9.6	69.7
67	K ₂ SO ₄ , glaserite	10.9	18.3	29.2
87	Na ₂ CO ₃ ·1H ₂ O, Na ₂ CO ₃ , K ₂ CO ₃	26.8	124.0	150.8
88	K ₂ CO ₃ ·½H ₂ O, Na ₂ CO ₃ , K ₂ CO ₃	13.2	152.0	165.2
48	K ₂ CO ₃ ·½H ₂ O, K ₂ SO ₄	157.9	...	Trace	157.9
19	Na ₂ CO ₃ ·1½H ₂ O, burkeite	75.4	...	8.0	...	83.4
20	Na ₂ SO ₄ , burkeite	21.4	...	46.5	...	67.9
103	Na ₂ CO ₃ ·1H ₂ O, Na ₂ CO ₃ , K ₂ CO ₃ , K ₂ SO ₄ ..	25.8	123.9	Trace	...	149.7
104	K ₂ CO ₃ ·½H ₂ O, Na ₂ CO ₃ , K ₂ CO ₃ , K ₂ SO ₄ ..	12.3	152.6	Trace	...	164.9
105	Na ₂ SO ₄ , burkeite, glaserite	11.6	9.0	54.6	...	75.2
106	Na ₂ CO ₃ ·1H ₂ O, K ₂ SO ₄ , glaserite	50.8	49.6	1.5	...	101.9
107	Na ₂ CO ₃ ·1H ₂ O, burkeite, glaserite	64.6	13.4	11.1	...	89.1

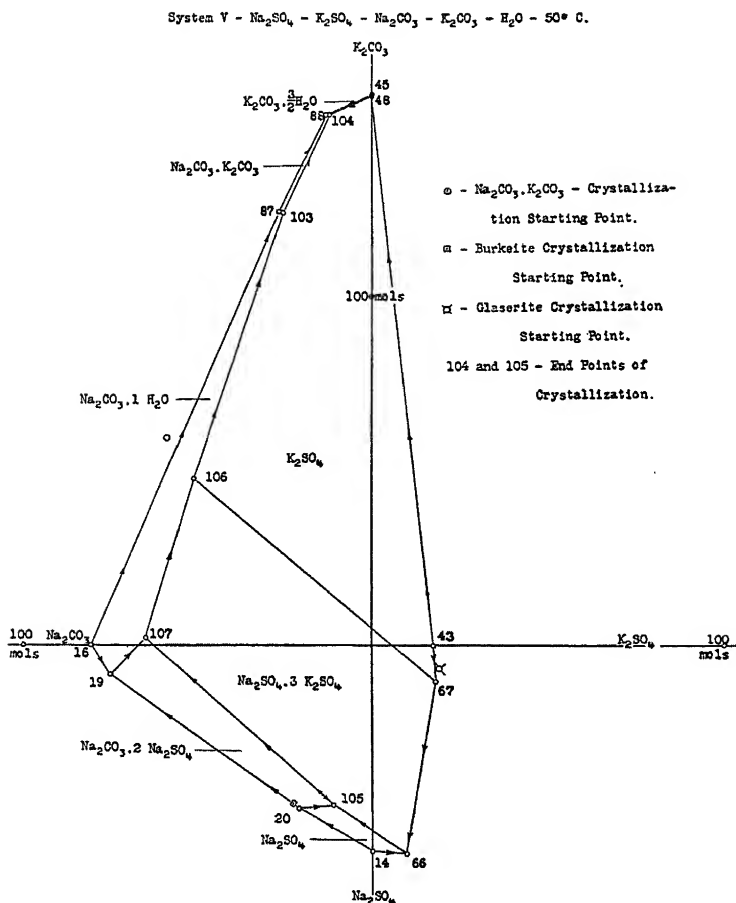


DIAGRAM 15.

SYSTEM V—75° C.

(Diagram 16)

Point	Solid Phases	Grams per 100 Grams of Water				
		Na ₂ CO ₃	K ₂ CO ₃	Na ₂ SO ₄	K ₂ SO ₄	Total
23	Na ₂ SO ₄	43.9	...	43.9
50	K ₂ SO ₄	20.6	20.6
25	Na ₂ CO ₃ · 1H ₂ O	45.3	45.3
52	K ₂ CO ₃ · 1H ₂ O	136.4	136.4
72	Na ₂ SO ₄ , glaserite	44.4	11.7	56.1
73	K ₂ SO ₄ , glaserite	8.1	21.8	29.9
92	Na ₂ CO ₃ · 1H ₂ O, Na ₂ CO ₃ , K ₂ CO ₃	18.0	94.2	112.2
93	K ₂ CO ₃ · 1H ₂ O, Na ₂ CO ₃ , K ₂ CO ₃	5.1	133.5	138.6
55	135.8	...	Trace	135.8
28	42.9	...	5.4	...	48.3
29	7.9	...	39.0	...	46.9
108 K ₂ SO ₄	17.1	93.0	Trace	...	110.1
109 K ₂ SO ₄	4.8	133.5	Trace	...	138.3
110	8.2	...	37.6	11.6	57.4
111	Na ₂ CO ₃ · 1H ₂ O, Na ₂ SO ₄ , glaserite	28.0	42.9	1.8	...	72.7
112	Na ₂ CO ₃ · 1H ₂ O, burkeite, glaserite	34.1	16.0	8.2	...	58.3

SYSTEM V—75° C.

(Diagram 16)

Point	Solid Phases	Mols per 1,000 Mols of Water				
		Na ₂ CO ₃	K ₂ CO ₃	Na ₂ SO ₄	K ₂ SO ₄	Total
23	Na ₂ SO ₄	55.6	...	55.6
50	K ₂ SO ₄	21.3	21.3
25	Na ₂ CO ₃ · 1H ₂ O	77.0	77.0
52	177.7	177.7
72	56.3	12.0	68.3
73	10.3	22.6	32.9
92	Na ₂ CO ₃ , K ₂ CO ₃	30.6	122.6	153.2
93	Na ₂ CO ₃ , K ₂ CO ₃	8.6	173.9	182.5
55	176.9	...	Trace	176.9
28 te	72.8	...	6.8	...	79.6
29	13.4	...	49.4	...	62.8
108 s, K ₂ CO ₃ , K ₂ SO ₄	29.0	121.2	Trace	...	150.2
109 K ₂ CO ₃ , K ₂ SO ₄	8.2	173.8	Trace	...	182.0
110 erite	13.9	...	47.6	11.9	73.4
111 glaserite	47.5	55.9	2.2	...	105.6
112	Na ₂ CO ₃ · 1H ₂ O, burkeite, glaserite	58.0	20.8	10.3	...	89.1

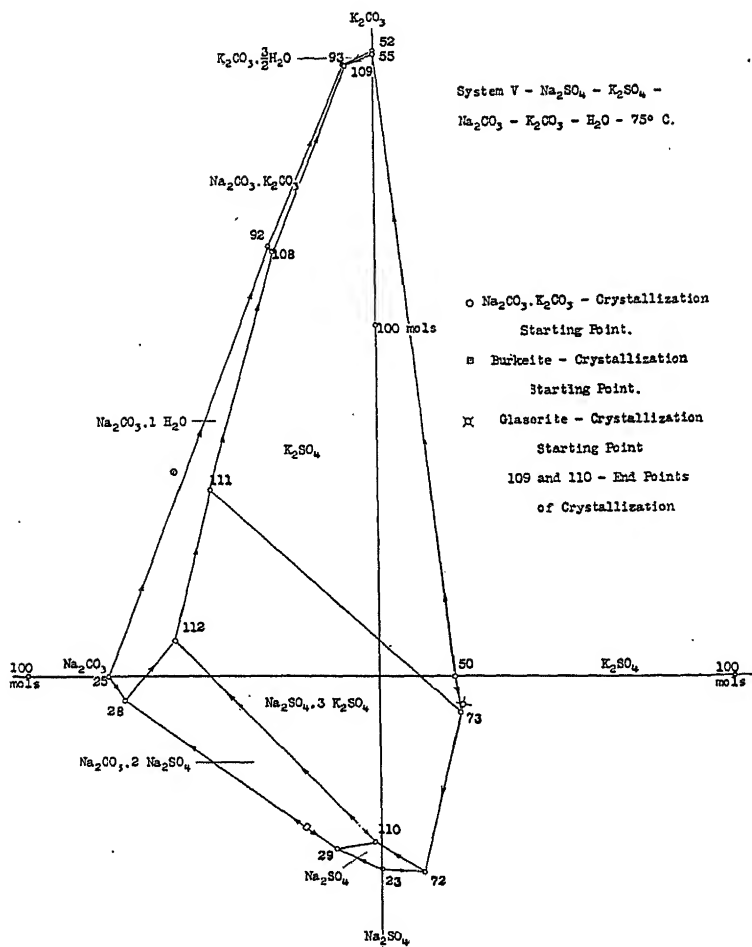


DIAGRAM 16.

SYSTEM VI

Sodium Chloride, Potassium Chloride, Sodium Sulfate, Potassium Sulfate, Sodium Carbonate, Potassium Carbonate, Water

(Diagrams 17, 18, 19, 20, 21, 22, 23, 24)

We come now to a five-component system, having already examined the five four-component systems which form its boundaries. We have seen that a two-component system of one salt and water may be represented at a given temperature by a single straight line, a three-component one by a plane surface containing and bounded by two two-component lines, a four-component one by a solid bounded by three or four three-component surfaces. By analogy we should expect to represent this five-component system by a figure in the fourth dimension containing and bounded by the five four-component solid systems previously discussed.

There are several serious objections to diagramming in and making deductions from figures in space of four and more dimensions, among which it is sufficient in this case to mention the mental deficiency of the writer, and probably of some of the readers. The difficulty, however, is only in the representation of the data, not in their determination. We can still obtain the analytical compositions of solutions at any univariant point and along all divariant lines, but at a univariant point in a five-component system containing water there are present four solid phases, and along a divariant line there are present three solid phases, and an area bounded by divariant lines now represents complete saturation with two solid phases. If we select only those parts of this five-component system that are completely saturated with one component, for example NaCl, we may represent the relationships to advantage in three dimension space with diagrams of the same type that we have been using. Diagram 17 shows that part of the system at 20° C. that is completely saturated with NaCl. Point 57 on this diagram represents 17.9 mols K_2Cl_2 , 46.1 mols Na_2Cl_2 and 1000 mols water, but only the K_2Cl_2 is plotted. Univariant point 114 represents equilibrium with four solid phases, KCl, $Na_2CO_3 \cdot 7H_2O$, glaserite and NaCl, of which only the first three are represented. This type of diagram has been exceedingly valuable in interpreting data because the simple limitation we have fixed, complete saturation with NaCl, is a very usual one in our plant practice.

Diagram 17 is interesting too because it so closely approximates the equilibrium conditions of Searles Lake brine as a whole. The temperature 20° C. is only 2.5° below the usual lake brine temperature, and the components given represent nearly 95 per cent of the total solids in the brine. In fact all of the important constituents are here excepting borax (and metaborate) and bicarbonate. The divariant line from point 289 to point 290 represents equilibrium with NaCl, glaserite and hanksite, all of which are solid phases in the lake, and the small triangle approximately on that line near point 289 represents the composition of Searles Lake brine so far as this five-component system is concerned, in equilibrium with the three solid phases and nearly saturated with Na_2SO_4 .

If we connect points 288, 289 and 290, the enclosed field represents saturation with NaCl and hanksite. This is the stable equilibrium. It was reached in the laboratory and the limits of the field determined only after many attempts. In ordinary practice this equilibrium is never reached, but its place is taken by the metastable equilibrium indicated by point 113 and the dotted lines. At point 113 solution is in metastable equilibrium with glaserite, burkeite, Na_2SO_4 and NaCl.

Diagrams 18, 20, 22 and 24 show the system saturated with NaCl at 35° , 50° , 75° and 100° C. respectively. From a practical point of view our object is to concentrate the brine in such a way as to reach a high percentage of KCl in solution without losing any potassium salt on the way. Particularly we wish to avoid precipitation of glaserite. Diagram 17 indicates that evaporation at 20° C. would follow the divariant line from the triangle to point 290 precipitating hanksite, glaserite and NaCl, then to point 115 precipitating burkeite, glaserite and NaCl, then to point 114 precipitating $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$, glaserite and NaCl, after which no increase in KCl concentration could be obtained. At 35° we would reach the burkeite field and could precipitate considerable amounts of NaCl and burkeite before reaching the glaserite field on the line between points 116 and 118. At 50° and 75° conditions are still more favorable. It becomes apparent that our aim in concentration should be to approach as near as possible to the KCl field without touching the glaserite field en route. So far as these diagrams now under consideration are concerned this is best accomplished at 100° in Diagram 24 where we would precipitate burkeite and NaCl across the whole field aiming at point 137 or 138, and having always enough Na_2CO_3 present to prevent touching the glaserite field in transit along the line between points 136 and 138. We thus theoretically evaporate four-fifths of the water, multiply the potash concentration by 5, precipitate most

of the other salts and lose no potash in the precipitated salts—
theoretically.

Diagrams 19, 21, 23 represent a portion of the five-component system at 35°, 50°, and 75° C., all points saturated with KCl. These diagrams and others not published indicate of course what will happen when we cool our concentrated solution in order to precipitate and recover the KCl. They also indicate, if one needs the indication, the difficulty of recovering potassium carbonate by evaporation from materials we have available.

These eight diagrams naturally give a very incomplete picture of the five-component system. They cover only a small part of it at a very few temperatures, but we have no more to offer now.

SYSTEM VI—20° C.

(Diagram 17)

Point	Solid Phases	Grams per 100 Grams of Water						
		NaCl	KCl	Na ₂ SO ₄	K ₂ SO ₄	Na ₂ CO ₃	K ₂ CO ₃	Total
*113	NaCl, Na ₂ SO ₄ , burkeite, glaserite....	30.2	...	11.7	...	2.5	6.5	50.9
114	NaCl, Na ₂ SO ₄ , burkeite, glaserite....	26.8	...	2.7	...	14.2	12.2	55.9
115	NaCl, Na ₂ CO ₃ ·7H ₂ O, burkeite, glaserite	25.2	...	5.8	...	15.8	8.1	54.9
288	NaCl, Na ₂ SO ₄ , burkeite, hanksite	27.6	...	10.6	...	7.1	1.3	46.6
289	NaCl, Na ₂ SO ₄ , hanksite, glaserite	26.3	7.0	11.9	...	3.3	...	48.5
290	NaCl, burkeite, hanksite, glaserite	26.0	...	6.6	...	13.6	8.0	54.2

* Metastable point.

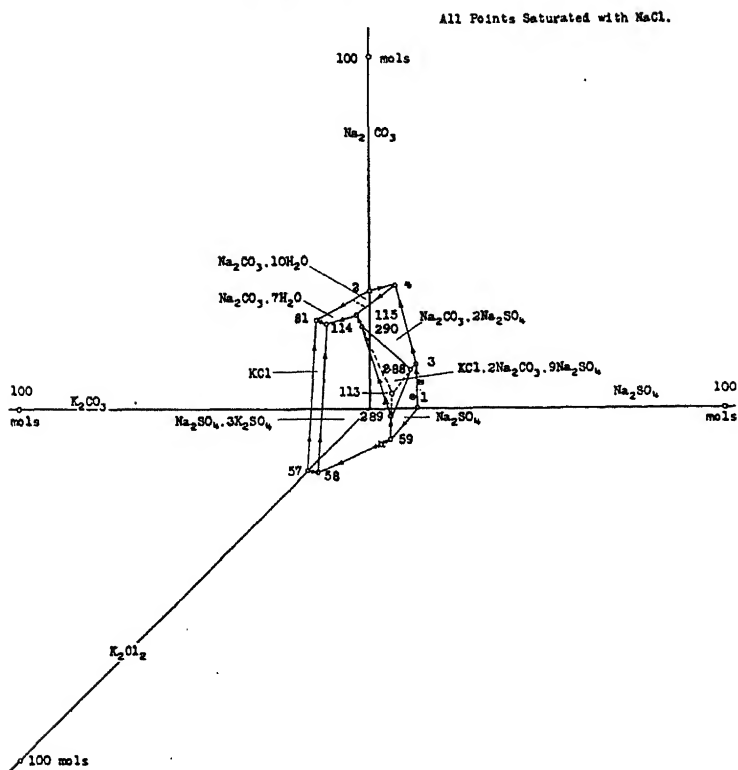
SYSTEM VI—20° C.

(Diagram 17)

Point	Solid Phases	Mols per 1,000 Mols of Water						
		Na ₂ Cl ₂	K ₂ Cl ₂	Na ₂ SO ₄	K ₂ SO ₄	Na ₂ CO ₃	K ₂ CO ₃	Total
*113	NaCl, Na ₂ SO ₄ , burkeite, glaserite....	46.6	...	14.8	...	4.2	8.5	74.1
114	NaCl, KCl, Na ₂ CO ₃ ·7H ₂ O, glaserite..	41.2	...	3.4	...	24.2	15.9	84.7
115	NaCl, Na ₂ CO ₃ ·7H ₂ O, burkeite, glaserite	38.9	...	7.4	...	26.8	10.6	83.7
288	NaCl, Na ₂ SO ₄ , burkeite, hanksite	42.5	...	13.4	...	12.0	1.7	69.6
289	NaCl, Na ₂ SO ₄ , hanksite, glaserite	40.5	8.4	15.1	...	5.7	...	69.7
290	NaCl, burkeite, hanksite, glaserite	40.1	...	8.4	...	23.1	10.4	82.0

* Metastable point.

SYSTEM VI: $\text{NaCl} - \text{KCl} - \text{Na}_2\text{SO}_4 - \text{K}_2\text{SO}_4 - \text{Na}_2\text{CO}_3 - \text{K}_2\text{CO}_3 - \text{H}_2\text{O}$; 20°C .



- m - Burkeite Crystallization Starting Point
- u - Glauberite Crystallization Starting Point
- e - Hanksite Crystallization Starting Point
- 114 - End Point of Crystallization
- ▲ - Approximate Point for Searles Lake Brine.

DIAGRAM 17.

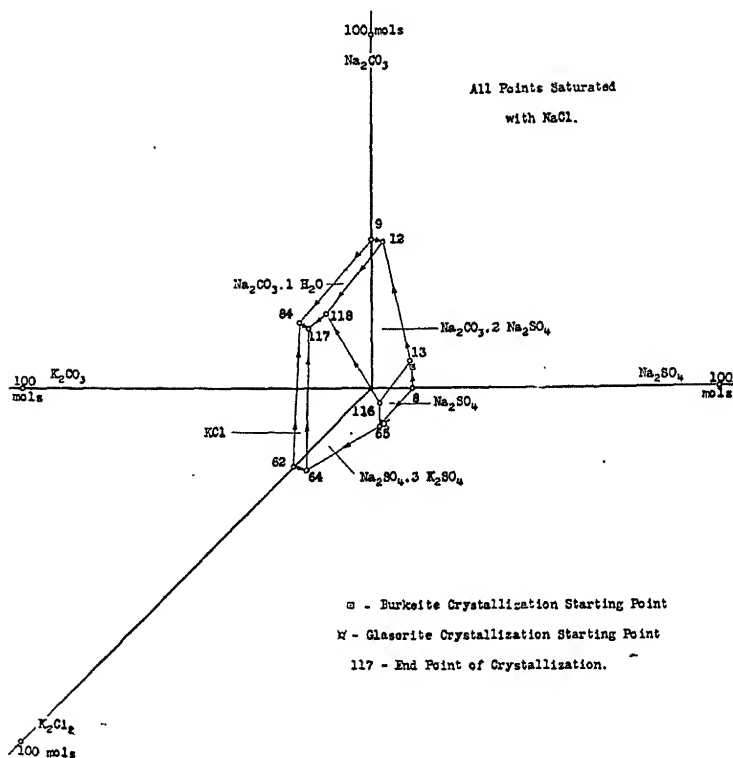
System VI - NaCl - KCl - Na₂SO₄ - K₂SO₄ - Na₂CO₃ - K₂CO₃ - H₂O - 35° C.

DIAGRAM 18.

SYSTEM VI—35° C.

(Diagrams 18 and 19)

Point	Solid Phases	Grams per 100 Grams of Water						
		NaCl	KCl	Na ₂ SO ₄	K ₂ SO ₄	Na ₂ CO ₃	K ₂ CO ₃	Total
116	NaCl, Na ₂ SO ₄ , burckite, glaserite	31.0	3.6	10.4	5.4	50.4
117	NaCl, Na ₂ SO ₄ , burckite, glaserite	29.5	...	2.8	...	10.2	16.3	58.8
118	NaCl, Na ₂ SO ₄ , burckite, glaserite	28.8	...	3.3	...	12.8	13.7	58.6
119	KCl, K ₂ SO ₄ , Na ₂ CO ₃ · 1H ₂ O, glaserite	...	12.9	...	0.9	30.6	23.7	68.1
120	KCl, K ₂ SO ₄ , Na ₂ CO ₃ · 1H ₂ O, Na ₂ CO ₃ · K ₂ CO ₃	...	2.9	...	Trace	14.5	94.6	112.0
121	KCl, K ₂ SO ₄ , K ₂ CO ₃ · 1H ₂ O, Na ₂ CO ₃ · K ₂ CO ₃	...	2.7	...	Trace	9.1	107.8	119.6

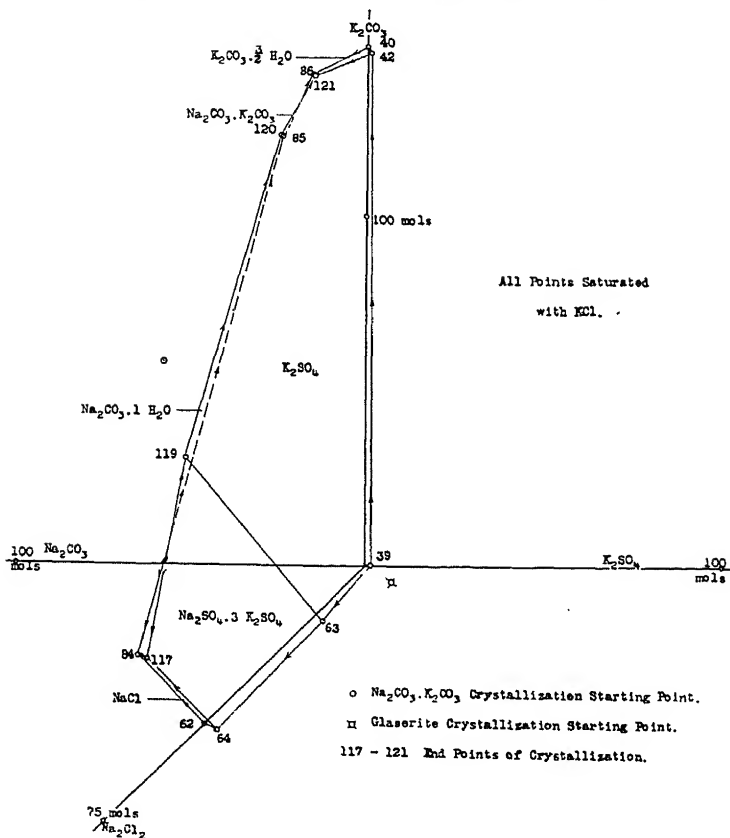
System VI - NaCl - KCl - Na₂SO₄ - K₂SO₄ - Na₂CO₃ - K₂CO₃ - H₂O - 35° C.

DIAGRAM 19.

SYSTEM VI—35° C.
(Diagrams 18 and 19)

Point	Solid Phases	Mols per 1,000 Mols of Water						
		Na ₂ Cl ₂	K ₂ Cl ₂	Na ₂ SO ₄	K ₂ SO ₄	Na ₂ CO ₃	K ₂ CO ₃	Total
116	NaCl, Na ₂ SO ₄ , burkeite, glaserite	47.7	4.3	13.2	7.0	72.2
117	NaCl, K ₂ SO ₄ , Na ₂ CO ₃ .1H ₂ O, glaserite...	45.4	...	3.5	...	17.4	21.2	87.5
118	NaCl, Na ₂ CO ₃ .1H ₂ O, burkeite, glaserite	44.3	...	4.2	...	21.7	17.9	88.1
119	KCl, K ₂ SO ₄ , Na ₂ CO ₃ .1H ₂ O, glaserite.	...	15.6	...	0.9	52.0	30.9	99.4
120	KCl, K ₂ SO ₄ , Na ₂ CO ₃ .1H ₂ O, Na ₂ CO ₃ .K ₂ CO ₃	...	3.5	...	Trace	24.6	123.2	151.3
121	KCl, K ₂ SO ₄ , K ₂ CO ₃ .1H ₂ O, Na ₂ CO ₃ .K ₂ CO ₃	...	3.3	...	Trace	15.5	140.4	159.2

106 INDUSTRIAL DEVELOPMENT OF SEARLES LAKE BRINES

System VI - NaCl - KCl - Na₂SO₄ - K₂SO₄ - Na₂CO₃ - K₂CO₃ - H₂O - 50° C.

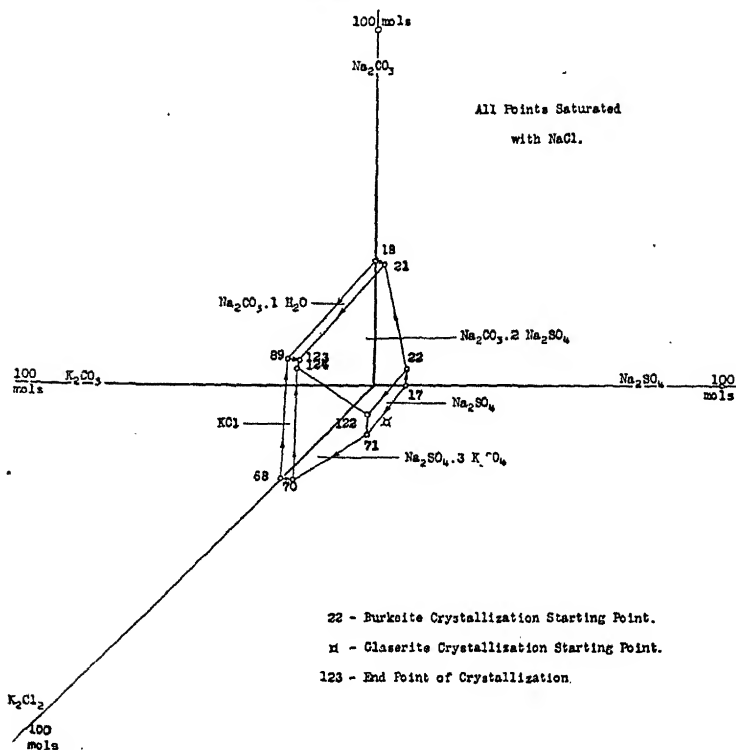


DIAGRAM 20.

SYSTEM VI—50° C.
 (Diagrams 20 and 21)

Point	Solid Phases	Grams per 100 Grams of Water						
		NaCl	KCl	Na ₂ SO ₄	K ₂ SO ₄	Na ₂ CO ₃	K ₂ CO ₃	Total
122	NaCl, Na ₂ SO ₄ , burkeite, glaserite . . .	30.8	7.1	9.7	4.1	51.7
123	NaCl, KCl, Na ₂ CO ₃ .1H ₂ O, burkeite ..	34.0	...	3.0	...	4.3	19.5	60.8
124	NaCl, KCl, burkeite, glaserite	34.7	...	3.0	...	3.0	20.2	60.9
125	KCl, K ₂ SO ₄ , Na ₂ CO ₃ .1H ₂ O, glaserite..	...	16.6	...	1.2	27.6	25.6	71.0
126	KCl, K ₂ SO ₄ , Na ₂ CO ₃ .1H ₂ O, Na ₂ CO ₃ .K ₂ CO ₃	...	4.6	...	Trace	15.8	92.6	113.0
127	KCl, K ₂ SO ₄ , K ₂ CO ₃ .1H ₂ O, Na ₂ CO ₃ .K ₂ CO ₃	...	3.6	...	Trace	8.5	114.8	126.9
128	KCl, Na ₂ CO ₃ .1H ₂ O, burkeite, glaserite	18.3	19.4	...	3.0	19.6	...	60.3

108 INDUSTRIAL DEVELOPMENT OF SEARLES LAKE BRINES

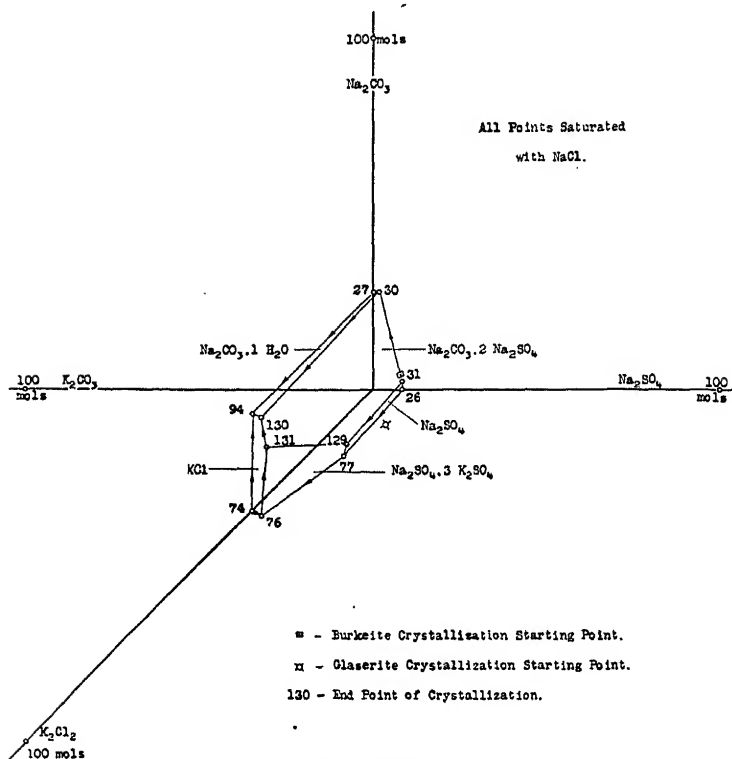
System VI - NaCl - KCl - Na₂SO₄ - K₂SO₄ - Na₂CO₃ - K₂CO₃ - H₂O - 75° C.

DIAGRAM 22.

SYSTEM VI—75° C.
(Diagrams 22 and 23)

Point	Solid Phases	Grams per 100 Grams of Water						
		NaCl	KCl	Na ₂ SO ₄	K ₂ SO ₄	Na ₂ CO ₃	K ₂ CO ₃	Total
129	NaCl, Na ₂ SO ₄ , burkeite, glaserite . . .	30.0	13.2	9.2	2.0	54.4
130	NaCl, KCl, Na ₂ CO ₃ .1H ₂ O, burkeite ..	35.4	6.7	2.4	20.6	65.1
131	NaCl, KCl, burkeite, glaserite	32.2	13.8	3.5	14.0	63.5
132	KCl, K ₂ SO ₄ , Na ₂ CO ₃ .1H ₂ O, glaserite..	...	22.8	...	1.9	25.3	26.7	76.7
133	KCl, K ₂ SO ₄ , Na ₂ CO ₃ .1H ₂ O, Na ₂ CO ₃ .K ₂ CO ₃	...	7.4	...	Trace	16.7	87.9	112.0
134	KCl, K ₂ SO ₄ , K ₂ CO ₃ .3H ₂ O, Na ₂ CO ₃ .K ₂ CO ₃	...	4.9	...	Trace	3.5	133.3	141.7
135	KCl, Na ₂ CO ₃ .1H ₂ O, burkeite, glaserite	14.3	28.6	...	3.5	19.4	...	65.8

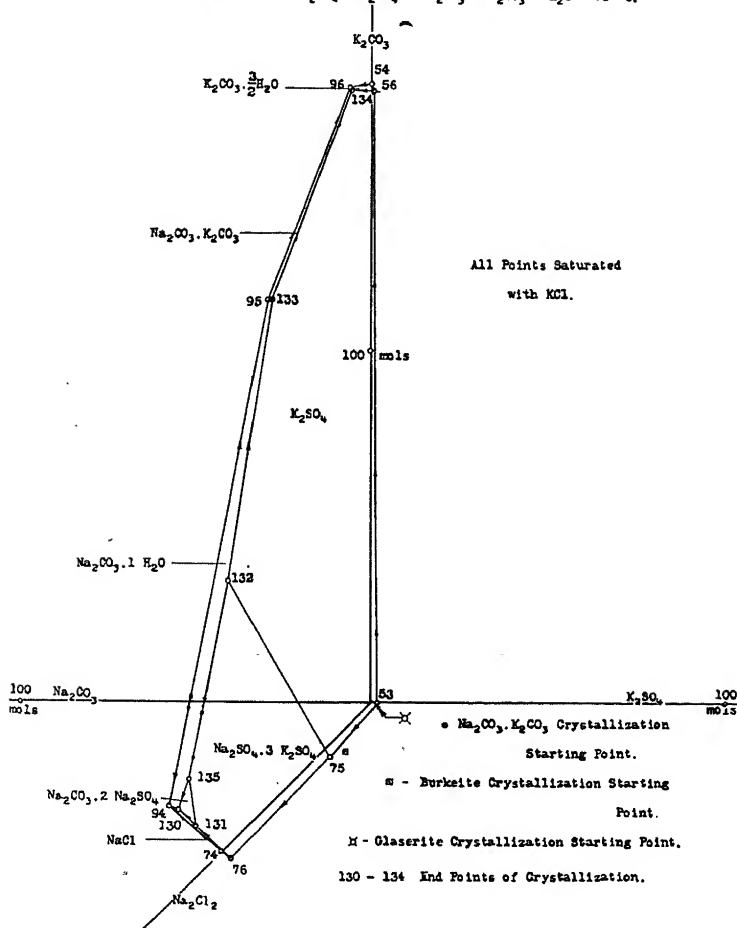
System VI - NaCl - KCl - Na₂SO₄ - K₂SO₄ - Na₂CO₃ - K₂CO₃ - H₂O - 75° C.

DIAGRAM 23.

SYSTEM VI—75° C.
(Diagrams 22 and 23)

Point	Solid Phases	Mols per 1,000 Mols of Water						
		Na ₂ Cl ₂	K ₂ Cl ₂	Na ₂ SO ₄	K ₂ SO ₄	Na ₂ CO ₃	K ₂ CO ₃	Total
129	NaCl, Na ₂ SO ₄ , burkeite, glaserite	46.2	15.9	11.7	2.6	76.4
130	NaCl, Na ₂ SO ₄ , burkeite	54.5	8.1	3.1	26.9	92.6
131	NaCl, Na ₂ SO ₄ , glaserite	49.5	16.7	4.5	18.2	88.9
132	KCl, Na ₂ SO ₄ , glaserite	...	27.5	...	2.0	42.9	34.8	107.2
133	KCl, Na ₂ SO ₄ , Na ₂ CO ₃ , K ₂ CO ₃	...	8.9	...	Trace	28.3	114.5	151.7
134	KCl, K ₂ SO ₄ , K ₂ CO ₃ , Na ₂ CO ₃	...	5.9	...	Trace	5.9	173.6	185.4
135	KCl, Na ₂ CO ₃ ·1H ₂ O, burkeite, glaserite	22.0	34.5	...	3.6	33.0	...	93.1

SYSTEM VI—100° C.

(Diagram 24)

Point	Solid Phases	Grams per 100 Grams of Water						
		NaCl	KCl	Na ₂ SO ₄	K ₂ SO ₄	Na ₂ CO ₃	K ₂ CO ₃	Total
136	NaCl, Na ₂ SO ₄ , burkeite, glaserite	30.2	17.8	8.9	1.3	58.2
137	NaCl, Na ₂ SO ₄ , burkeite ..	33.9	15.9	2.5	17.9	70.2
138	NaCl, Na ₂ SO ₄ , glaserite	31.0	26.1	3.7	9.6	70.4

SYSTEM VI—100° C.

(Diagram 24)

Point	Solid Phases	Mols per 1,000 Mols of Water						Total
		Na ₂ Cl ₂	K ₂ Cl ₂	Na ₂ SO ₄	K ₂ SO ₄	Na ₂ CO ₃	K ₂ CO ₃	
136	NaCl, Na ₂ SO ₄ , burkeite, glaserite	46.5	21.4	11.3	1.7	80.9
137	NaCl, KCl, Na ₂ SO ₄ , burkeite ..	52.2	19.2	3.1	23.3	97.8
138	NaCl, Na ₂ SO ₄ , glaserite	47.7	31.5	4.7	12.5	96.4

SYSTEM VII *

Sodium Chloride, Sodium Carbonate, Sodium Metaborate, Water
(Diagram 25)

This is the first of the five four-component systems which must be examined in studying the five-component system water and the chloride, carbonate, bicarbonate, borate and metaborate of sodium. The diagrams are all for 35° C. or less. At high temperatures NaHCO_3 is not stable in solution, but in any case our chief interest centered in the lower temperature range. The possibility of the existence of other hydrates besides those given in the diagrams is not entirely excluded. No others were found but no special search was made for them.

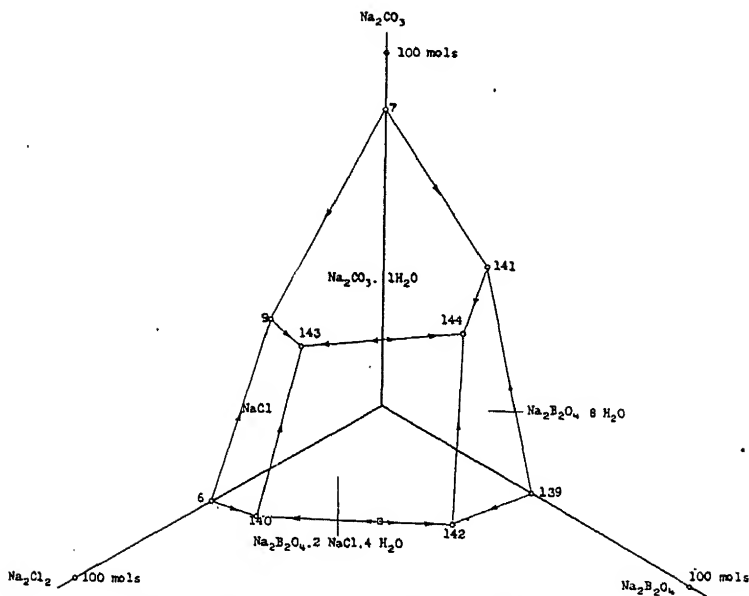
Diagram 25 represents water and the chloride, carbonate and metaborate of sodium at 35° C., four components. The fields for NaCl , $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, and $\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$, present no unusual features, except the tendency of metaborate to form supersaturated solutions, and its sluggishness in crystallizing. But the fourth field represents an entirely new double salt, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$, stable in contact with mixed solution of chloride and metaborate, with or without carbonate, over a very wide range of concentrations. Both chloride and metaborate are present in Searles Lake brine, and in fact this double salt would appear in large quantity if the brine ever reached the end point of crystallization. In plant mother liquors the metaborate naturally reaches a much higher concentration than it has in lake brine, and at points 140 or 143 in Diagram 25 only 5 or 6 per cent metaborate is necessary to cause precipitation of the double salt. Hence the necessity of a knowledge of its activities is apparent. Whether the end point of crystallization shall be point 143 or point 144 depends of course on the relative initial concentrations of chloride and metaborate.

SYSTEM VII—35° C.

(Diagram 25)

Point	Solid Phases	Grams per 100 Grams of Water			
		NaCl	Na_2CO_3	$\text{Na}_2\text{B}_2\text{O}_4$	Total
6	NaCl	36.3	36.3
7	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$...	49.2	...	49.2
139		35.7	35.7
9		24.0	24.8	...	48.8
140		33.5	...	8.3	41.8
141		...	33.0	24.2	57.2
142	$4\text{H}_2\text{O}$	13.7	...	32.8	46.5
143	$\text{NaCl} \cdot 4\text{H}_2\text{O}$	23.2	22.8	6.8	52.8
144	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$	6.9	26.2	26.9	60.0

* Systems VII to XII inclusive are the work of William E. Burke.

System VII - $\text{NaCl} - \text{Na}_2\text{CO}_3 - \text{Na}_2\text{B}_2\text{O}_4 - \text{H}_2\text{O} - 35^\circ\text{C}.$  m $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2 \text{NaCl} \cdot 4 \text{H}_2\text{O}$ - Crystallization Starting Point.

143-144 - End Points of Crystallization.

DIAGRAM 25.

SYSTEM VII— $35^\circ\text{C}.$

(Diagram 25)

Point	Solid Phases	Mols per 1,000 Mols of Water			
		Na_2Cl_2	Na_2CO_3	$\text{Na}_2\text{B}_2\text{O}_4$	Total
6	NaCl	55.8	55.8
7	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$...	83.7	...	83.7
139	Na_2CO_3	48.7	48.7
9	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	37.0	42.1	...	79.1
140	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	51.6	...	11.3	62.9
141	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$...	56.1	33.0	89.1
142	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	21.1	...	44.8	65.9
143	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	35.8	38.7	9.3	83.8
144	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	10.7	44.6	36.6	91.9

SYSTEM VIII

Sodium Chloride, Sodium Bicarbonate, Borax, Water

(Diagram 26)

This is another four-component system like the previous one, excepting that it has bicarbonate and borax instead of carbonate and metaborate. Neither bicarbonate nor borax is very soluble at 35° C., as shown in Diagram 26, nor does the presence of either one materially affect the solubility of the other, but the addition of NaCl will precipitate over 80 per cent of the bicarbonate and over 50 per cent of the borax from saturated solutions.

SYSTEM VIII—35° C.

(Diagram 26)

Point	Solid Phases	Grams per 100 Grams of Water			
		NaCl	NaHCO ₃	Na ₂ B ₄ O ₇	Total
6	NaCl	36.3	36.3
145	NaHCO ₃	11.7	...	11.7
146	Na ₂ B ₄ O ₇ · 10H ₂ O	5.3	5.3
147	NaCl, NaHCO ₃	35.2	2.0	...	37.2
148	NaCl, Na ₂ B ₄ O ₇ · 10H ₂ O	35.5	...	2.2	37.7
149	NaHCO ₃ , Na ₂ B ₄ O ₇ · 10H ₂ O	12.6	4.6	17.2
150	NaCl, NaHCO ₃ , Na ₂ B ₄ O ₇ · 10H ₂ O	34.8	2.1	2.5	39.4

SYSTEM VIII—35° C.

(Diagram 26)

Point	Solid Phases	Mols per 1,000 Mols of Water			
		Na ₂ Cl ₂	NaHCO ₃	$\frac{\text{Na}_2\text{B}_4\text{O}_7}{2}$	Total
6	NaCl	55.8	55.8
145	NaHCO ₃	25.2	...	25.2
146	Na ₂ B ₄ O ₇ · 10H ₂ O	9.5	9.5
147	NaCl, NaHCO ₃	54.2	4.3	...	58.5
148	NaCl, Na ₂ B ₄ O ₇ · 10H ₂ O	54.6	...	3.9	58.5
149	NaHCO ₃ , Na ₂ B ₄ O ₇ · 10H ₂ O	27.0	8.1	35.1
150	NaCl, NaHCO ₃ , Na ₂ B ₄ O ₇ · 10H ₂ O	53.6	4.6	4.4	62.6

System VIII - NaCl - NaHCO_3 - $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ - H_2O - 35°C .

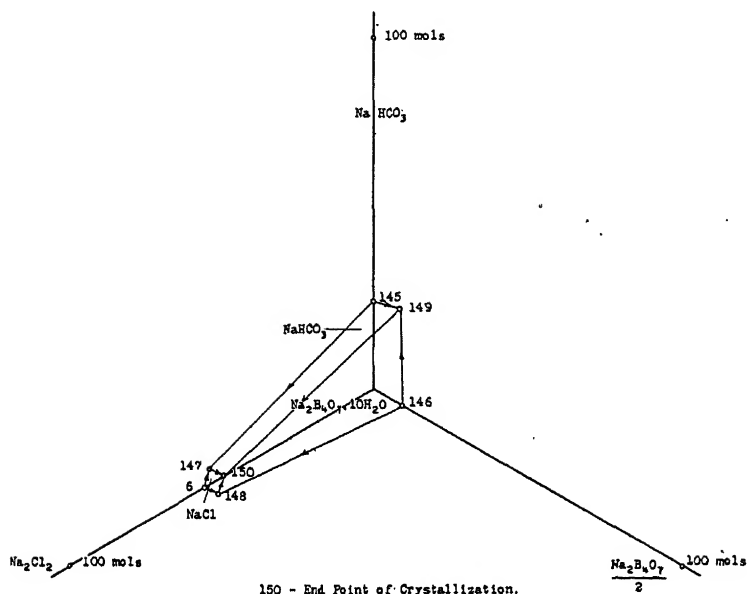


DIAGRAM 26.

SYSTEM IX

Sodium Chloride, Sodium Carbonate, Sodium Bicarbonate, Water

(Diagrams 27, 28)

Water and the chloride, carbonate and bicarbonate of sodium form a four-component system. In Diagram 27 we have the story of the double salt trona at 20° C. The field lies between the lines connecting points 247, 248, and 252. Considering the widespread occurrence of trona in many parts of the world it is rather remarkable that this double

SYSTEM IX—20° C.

(Diagram 27)

Point	Solid Phases	Grams per 100 Grams of Water			
		NaHCO ₃	Na ₂ CO ₃	NaCl	Total
236	NaHCO ₃	9.6	9.6
237	Na ₂ CO ₃ ·10H ₂ O	21.5	...	21.5
239	NaCl	36.0	36.0
2	Na ₂ CO ₃ ·10H ₂ O, NaCl	19.8	25.4	45.2
*240	Na ₂ CO ₃ ·10H ₂ O, NaHCO ₃	5.1	21.6	...	26.7
...	NaHCO ₃	7.5	7.2	...	14.7
*244	NaHCO ₃ , NaCl	1.4	...	35.8	37.2
*247	Na ₂ CO ₃ ·10H ₂ O, NaHCO ₃ , trona	4.4	20.7	2.8	27.9
...	Na ₂ CO ₃ ·10H ₂ O, trona	3.4	17.6	10.4	31.4
...	Na ₂ CO ₃ ·10H ₂ O, trona	1.5	17.4	19.3	38.3
*248	Na ₂ CO ₃ ·10H ₂ O, NaCl, trona	0.9	19.6	25.6	46.1
...	Na ₂ CO ₃ ·10H ₂ O	18.0	9.9	27.9
...	Na ₂ CO ₃ ·10H ₂ O	17.4	17.2	34.6
...	NaCl, trona	1.0	12.1	29.1	42.2
*252	NaCl, NaHCO ₃ , trona	2.1	3.6	32.9	38.6
...	NaHCO ₃ , trona	3.9	18.7	7.7	30.3
...	NaHCO ₃ , trona	3.7	7.8	17.5	29.0

* Data taken from Freeth, *Trans. Royal Society*, 233A, 35 (1922).

SYSTEM IX—20° C.

(Diagram 27)

Point	Solid Phases	Mols per 1,000 Mols of Water			
		NaHCO ₃	Na ₂ CO ₃	Na ₂ Cl ₂	Total
236	NaHCO ₃	20.6	20.6
237	Na ₂ CO ₃ ·10H ₂ O	36.5	...	36.5
239	NaCl	55.5	55.5
2	Na ₂ CO ₃ ·10H ₂ O, NaCl	33.6	39.1	72.7
*240	Na ₂ CO ₃ ·10H ₂ O, NaHCO ₃	10.9	36.7	...	47.6
...	NaHCO ₃	16.1	12.2	...	28.3
*244	NaHCO ₃ , NaCl	3.0	...	55.2	58.2
*247	Na ₂ CO ₃ ·10H ₂ O, NaHCO ₃ , trona	9.4	35.2	4.3	48.9
...	Na ₂ CO ₃ ·10H ₂ O, trona	7.3	29.9	16.0	53.2
...	Na ₂ CO ₃ ·10H ₂ O, trona	3.2	28.6	29.7	62.5
*248	Na ₂ CO ₃ ·10H ₂ O, NaCl, trona	1.9	33.3	39.4	74.6
...	Na ₂ CO ₃ ·10H ₂ O	30.6	15.3	45.9
...	Na ₂ CO ₃ ·10H ₂ O	29.6	26.5	56.1
...	NaCl, trona	2.1	20.5	44.8	67.4
*252	NaCl, NaHCO ₃ , trona	4.5	6.1	50.7	61.3
...	NaHCO ₃ , trona	8.4	31.8	11.9	52.1
...	NaHCO ₃ , trona	7.9	13.3	27.0	48.2

* Data taken from Freeth, *Trans. Royal Society* 233A, 35 (1922).

salt cannot be formed from carbonate and bicarbonate alone at 20°. The presence of NaCl is necessary for the stable equilibrium of trona with a solution of its constituents at that temperature. If we pass CO_2 into a saturated solution of Na_2CO_3 at 20° there will be no precipitate except NaHCO_3 . At 35°, however (Diagram 28), only trona will be precipitated, until over half of the carbonate has disappeared. Diagram 27 is one of the very few for which we had the pleasure of finding data already in the literature.

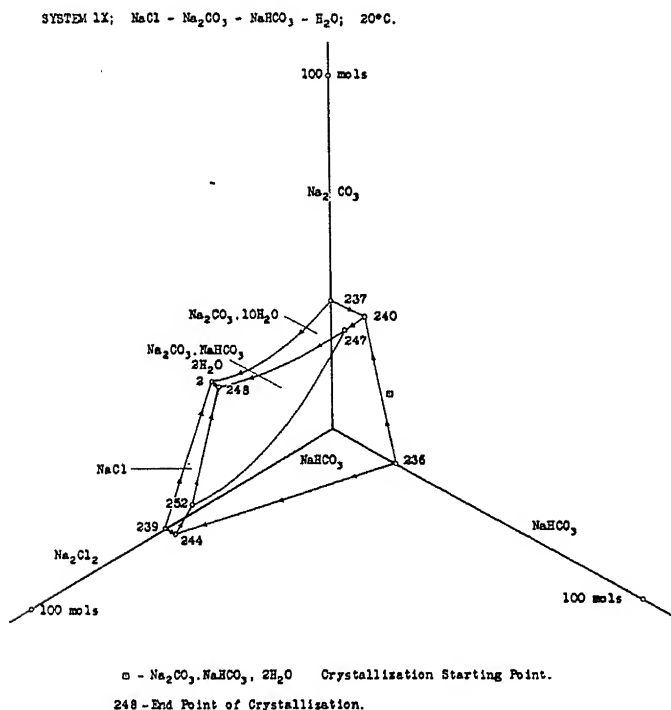


DIAGRAM 27.

SYSTEM IX—35° C.

(Diagram 28)

Point	Solid Phases	Grams per 100 Grams of Water			
		NaCl	Na ₂ CO ₃	NaHCO ₃	Total
6	NaCl	36.3	36.3
7	Na ₂ CO ₃ ·1H ₂ O	49.2	...	49.2
145	NaHCO ₃	11.7	11.7
9	NaCl, Na ₂ CO ₃ ·1H ₂ O	24.0	24.8	...	48.8
147	NaCl, NaHCO ₃	35.2	...	2.0	37.2
151	Na ₂ CO ₃ ·1H ₂ O, trona	49.2	0.8	50.0
152	NaHCO ₃ , trona	21.8	6.2	28.0
153	NaCl, Na ₂ CO ₃ ·1H ₂ O, trona	24.0	24.7	0.3	49.0
154	NaCl, NaHCO ₃ , trona	33.5	4.2	1.8	39.5

SYSTEM IX—35° C.

(Diagram 28)

Point	Solid Phases	Mols per 1,000 Mols of Water			
		Na ₂ Cl ₂	Na ₂ CO ₃	NaHCO ₃	Total
6	NaCl	55.8	55.8
7	Na ₂ CO ₃ ·1H ₂ O	83.7	...	83.7
145	NaHCO ₃	25.2	25.2
9	NaCl, Na ₂ CO ₃ ·1H ₂ O	37.0	42.1	...	79.1
147	NaCl, NaHCO ₃	54.2	...	4.3	58.5
151	Na ₂ CO ₃ ·1H ₂ O, trona	83.6	1.6	85.2
152	NaHCO ₃ , trona	37.1	13.3	50.4
153	NaCl, Na ₂ CO ₃ ·1H ₂ O, trona	37.0	42.0	0.7	79.7
154	NaCl, NaHCO ₃ , trona	51.6	7.2	4.0	62.8

System IX - $\text{NaCl} - \text{Na}_2\text{CO}_3 - \text{NaHCO}_3 - \text{H}_2\text{O} - 35^\circ\text{C}$.

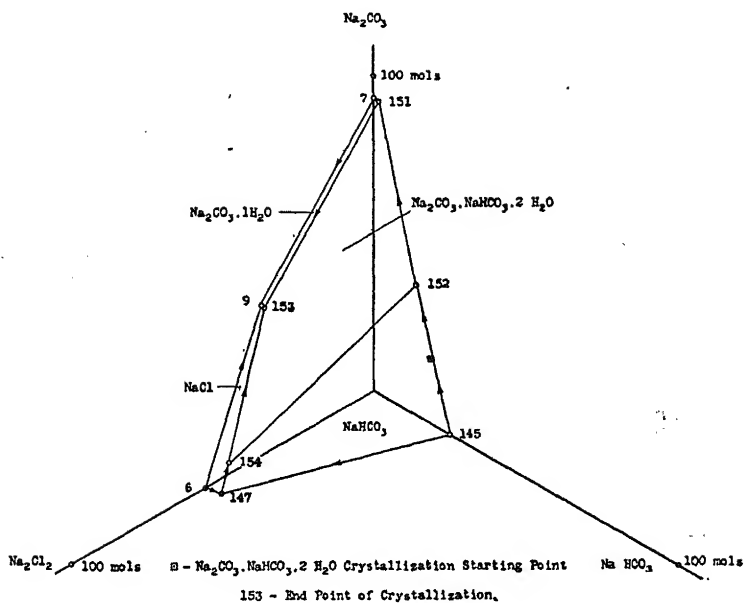


DIAGRAM 28.

SYSTEM X

Sodium Chloride, Borax, Sodium Metaborate, Water

(Diagrams 29, 30)

Water and the chloride, tetraborate, and metaborate of sodium form a four-component system. In Diagram 29 note the sharp curvature of the divariant line connecting points 266 and 262, the line of borax solubility in a solution of metaborate. The corresponding data sheet shows a minimum borax solubility at about 15 mols metaborate. In Diagram 30 at 35° C. the line connecting points 155 and 146 if accurately drawn would show the same curvature. At these two points the borax solu-

SYSTEM X—20° C.

(Diagram 29)

Point	Solid Phases	Grams per 100 Grams of Water			
		$\text{Na}_2\text{B}_4\text{O}_7$	$\text{Na}_2\text{B}_2\text{O}_4$	NaCl	Total
262	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	2.5	2.5
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	1.95	0.5	...	2.45
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	0.5	4.9	...	5.4
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	0.4	11.3	...	11.7
263	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$...	25.75	...	25.75
239	NaCl	36.0	36.0
266	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$	0.5	25.1	...	25.6
271	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$...	23.0	19.2	42.2
270	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$, NaCl	...	8.0	33.3	41.3
269	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, NaCl	0.9	...	36.0	36.9
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, NaCl	0.5	0.5	35.8	36.8
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, NaCl	0.3	2.3	34.7	37.3
276	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$	0.4	23.2	19.3	42.9
280	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$, NaCl	0.2	8.0	33.2	41.4

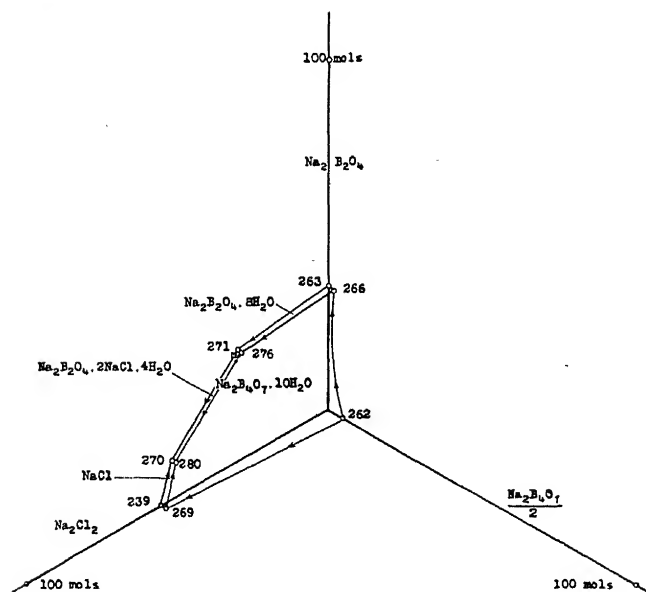
SYSTEM X—20° C.

(Diagram 29)

Point	Solid Phases	Mols per 1,000 Mols of Water			
		$\frac{\text{Na}_2\text{B}_4\text{O}_7}{2}$	$\text{Na}_2\text{B}_2\text{O}_4$	Na_2Cl_2	Total
262	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	4.46	4.46
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	3.48	0.68	...	4.16
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	0.9	6.7	...	7.6
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	0.7	15.4	...	16.1
263	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$...	35.14	...	35.14
239	NaCl	55.5	55.5
266	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$	1.0	34.3	...	35.3
271	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$...	31.4	29.6	61.0
270	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$, NaCl	...	10.9	51.3	62.2
269	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, NaCl	1.5	...	55.5	57.0
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, NaCl	0.8	0.7	55.2	56.7
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, NaCl	0.5	3.1	53.5	57.1
276	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$	0.6	31.6	29.7	61.9
280	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$, NaCl	0.3	10.9	51.2	62.4

bility is nearly 10 mols $\frac{\text{Na}_2\text{B}_4\text{O}_7}{2}$ per thousand mols water, while at an intermediate point it drops to about 3 mols. In general the divariant lines in our equilibrium work are approximately straight, and they are usually drawn straight in the diagrams. For our purpose the accurate location of univariant points was more important than a knowledge of the exact curvature of divariant lines. In both Diagrams 29 and 30 the metaborate chloride double salt recurs. This may be expected whenever chloride and metaborate are present in even moderately concentrated solution. Borax solubility changes rapidly with temperature. It more than doubles between 20° and 35° .

SYSTEM X; $\text{NaCl} - \text{Na}_2\text{B}_4\text{O}_7 - \text{Na}_2\text{B}_2\text{O}_4 - \text{H}_2\text{O}; 20^\circ\text{C}.$



□ - $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$, Crystallization Starting Point.

276 and 280 - End Points of Crystallization.

DIAGRAM 29.

SYSTEM X—35° C.

(Diagram 30)

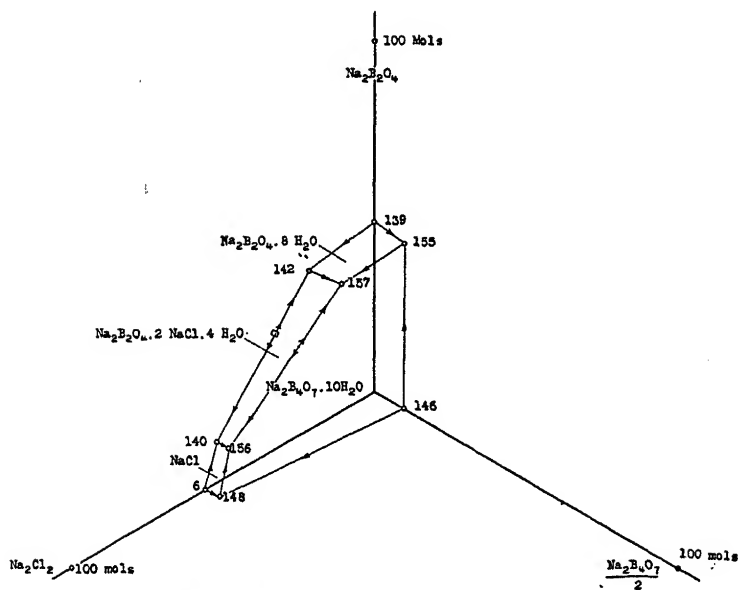
Point	Solid Phases	Grams per 100 Grams of Water			
		NaCl	Na ₂ B ₄ O ₇	Na ₂ B ₂ O ₄	Total
6	NaCl	36.3	36.3
146	Na ₂ B ₄ O ₇ ·10H ₂ O	5.3	...	5.3
139	Na ₂ B ₂ O ₄ ·8H ₂ O	35.7	35.7
148	NaCl, Na ₂ B ₄ O ₇ ·10H ₂ O	35.5	2.2	...	37.7
140	NaCl, Na ₂ B ₄ O ₇ ·2NaCl·4H ₂ O	33.5	...	8.3	41.8
155	Na ₂ B ₄ O ₇ ·10H ₂ O, Na ₂ B ₂ O ₄ ·8H ₂ O	5.6	34.8	40.4
142	Na ₂ B ₂ O ₄ ·8H ₂ O, Na ₂ B ₄ O ₇ ·2NaCl·4H ₂ O	13.7	...	32.8	46.5
156	NaCl, Na ₂ B ₄ O ₇ ·10H ₂ O, Na ₂ B ₂ O ₄ ·2NaCl·4H ₂ O	33.1	2.0	8.0	43.1
157	Na ₂ B ₄ O ₇ ·10H ₂ O, Na ₂ B ₂ O ₄ ·8H ₂ O, Na ₂ B ₂ O ₄ ·2NaCl·4H ₂ O	12.9	5.2	32.7	50.8

SYSTEM X—35° C.

(Diagram 30)

Point	Solid Phases	Mols per 1,000 Mols of Water			
		Na ₂ Cl ₂	$\frac{\text{Na}_2\text{B}_4\text{O}_7}{2}$	Na ₂ B ₂ O ₄	Total
6	NaCl	55.8	55.8
146	Na ₂ B ₄ O ₇ ·10H ₂ O	9.5	...	9.5
139	Na ₂ B ₂ O ₄ ·8H ₂ O	48.7	48.7
148	NaCl, Na ₂ B ₄ O ₇ ·10H ₂ O	54.6	3.9	...	58.5
140	NaCl, Na ₂ B ₄ O ₇ ·2NaCl·4H ₂ O	51.6	...	11.3	62.9
155	Na ₂ B ₄ O ₇ ·10H ₂ O, Na ₂ B ₂ O ₄ ·8H ₂ O	9.9	47.4	57.3
142	Na ₂ B ₂ O ₄ ·8H ₂ O, Na ₂ B ₄ O ₇ ·2NaCl·4H ₂ O	21.1	...	44.8	65.9
156	NaCl, Na ₂ B ₄ O ₇ ·10H ₂ O, Na ₂ B ₂ O ₄ ·2NaCl·4H ₂ O	51.0	3.5	11.0	65.5
157	Na ₂ B ₄ O ₇ ·10H ₂ O, Na ₂ B ₂ O ₄ ·8H ₂ O, Na ₂ B ₂ O ₄ ·2NaCl·4H ₂ O	19.9	9.2	44.7	73.8

System X - NaCl - $\text{Na}_2\text{B}_4\text{O}_7$ - $\text{Na}_2\text{B}_2\text{O}_4$ - H_2O - 35°C .



6 - $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2 \text{NaCl} \cdot 4 \text{H}_2\text{O}$ - Crystallization Starting Point.

156 and 157 - End Point of Crystallization.

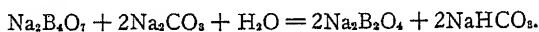
DIAGRAM 30.

SYSTEM XI

Sodium Carbonate, Sodium Bicarbonate, Sodium Tetraborate, Sodium Metaborate, Water

(Diagram 31)

Water and the carbonate, bicarbonate, tetraborate and metaborate of sodium form a four-component system. We may consider it as a reciprocal salt pair.



The method used in Diagram 31 is accordingly the one described under System III. Trona is the only double salt to appear.

SYSTEM XI—35° C.

(Diagram 31)

Point	Solid Phases	Grams per 100 Grams of Water				
		Na_2CO_3	NaHCO_3	$\text{Na}_2\text{B}_4\text{O}_7$	$\text{Na}_2\text{B}_2\text{O}_4$	Total
7	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	49.2	49.2
145	NaHCO_3	11.7	11.7
146	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	5.3	...	5.3
139	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$	35.7	35.7
141	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	33.0	24.2	57.2
151	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	49.2	0.8	50.0
149	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	12.6	4.6	...	17.2
152	NaHCO_3 , trona	21.8	6.2	28.0
155	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$	5.6	34.8	40.4
158	trona, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	41.4	...	3.4	10.0	54.8
159	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$	30.3	...	7.2	26.4	63.9
160	NaHCO_3 , $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, trona	21.2	6.4	4.0	...	31.6

SYSTEM XI—35° C.

(Diagram 31)

Point	Solid Phases	Mols per 1,000 Mols of Water				
		Na_2CO_3	NaHCO_3	$\frac{\text{Na}_2\text{B}_4\text{O}_7}{2}$	$\text{Na}_2\text{B}_2\text{O}_4$	Total
7	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	83.7	83.7
145	NaHCO_3	25.2	25.2
146	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	9.5	...	9.5
139	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$	48.7	48.7
141	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$	56.1	33.0	89.1
151	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, trona	83.6	1.6	85.2
149	NaHCO_3 , $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	27.0	8.1	...	35.1
152	NaHCO_3 , trona	37.1	13.3	50.4
155	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$	9.9	47.4	57.3
158	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, trona, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	70.4	...	6.0	13.6	90.0
159	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$	51.5	...	12.8	36.0	100.3
160	NaHCO_3 , $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, trona	36.0	13.8	7.0	...	56.8

System XI - Na_2CO_3 - NaHCO_3 - $\text{Na}_2\text{B}_4\text{O}_7$ - $\text{Na}_2\text{B}_2\text{O}_4$ - H_2O - 35°C .

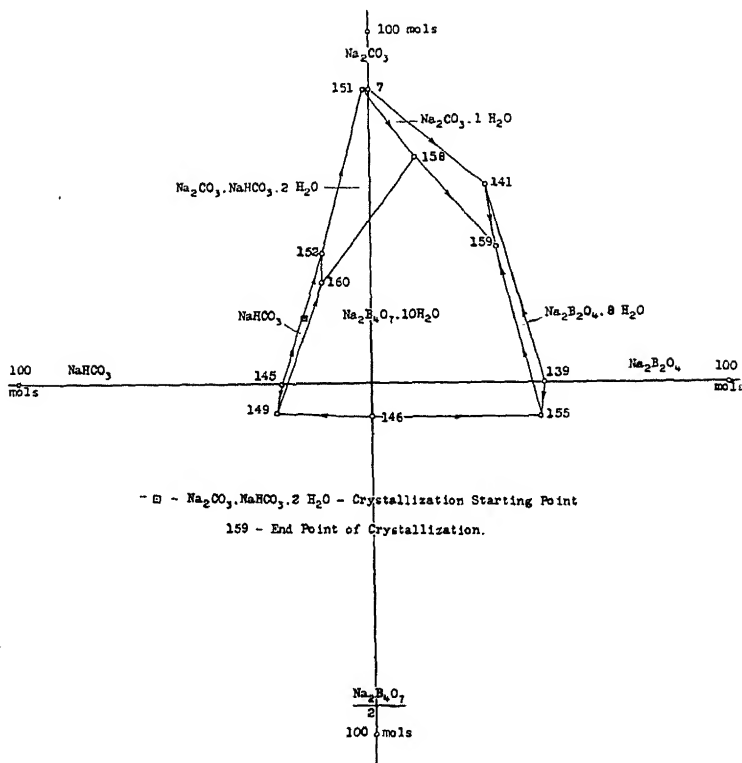


DIAGRAM 31.

SYSTEM XII

Sodium Chloride, Sodium Carbonate, Sodium Bicarbonate, Sodium Metaborate, Sodium Tetraborate, and Water

(Diagrams 32, 33, 34)

We have now examined the five four-component systems leading up to this five-component system of water and the chloride, carbonate, bicarbonate, tetraborate and metaborate of sodium. Only two parts of this system are shown at 35° C. and one of them at 20° C. Diagrams 32 and 33 show all points saturated with NaCl as we find it in lake brine, and Diagram 34 saturated with $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, as may occur in a plant liquor. System VI included all the important constituents of the lake brine except B_2O_3 and bicarbonate. System XII includes all except potassium and sulfate. In the former system the lake equilibrium was somewhere on the divariant line representing saturation with NaCl, hanksite and glaserite, and near point 289. In the latter it is on the line where NaCl, borax and trona are the solid phases, and near point 300. In the former we have indicated at point 14 the end point of crystallization, NaCl, Na_2CO_3 , KCl and glaserite; in the latter at point 302, NaCl, Na_2CO_3 , trona and the double metaborate chloride. Combining the two we determine that at the end point of crystallization the brine would be in equilibrium with those six salts, and this has been checked experimentally. By the time, however, that this end point is reached the brine has become so concentrated by evaporation that a seventh salt also appears, a double phosphate metaborate, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$, but this will be discussed later. In Systems VIII, X, XI, XII, one-half $\text{Na}_2\text{B}_4\text{O}_7$ has been used as the molar weight of borax in order to make it comparable with $\text{Na}_2\text{B}_2\text{O}_4$, a member of the other reciprocal salt pair.

From Diagrams 32 and 33 we see one effect of carbonating Searles Lake brine. This increases bicarbonate at the expense of carbonate, of course, and also increases borax at the expense of metaborate, and precipitates bicarbonate and borax if we are near natural brine temperature, or trona and borax and later bicarbonate at a slightly higher temperature. In either case we have borax in both precipitate and solution, which in general does not indicate a satisfactory operation.

SYSTEM XII—20° C.

(Diagram 32)

Point	Solid Phases	Grams per 100 Grams of Water					
		Na ₂ CO ₃	NaHCO ₃	Na ₂ B ₄ O ₇	Na ₂ B ₂ O ₄	NaCl	Total
290	NaCl, Na ₂ CO ₃ ·7H ₂ O, Na ₂ B ₂ O ₄ ·2NaCl·4H ₂ O	21.6	15.3	25.2	62.1
291	NaCl, Na ₂ B ₄ O ₇ ·10H ₂ O, NaHCO ₃	...	0.9	1.0	...	34.5	36.4
300	NaCl, Na ₂ B ₄ O ₇ ·10H ₂ O, NaHCO ₃ , trona	2.1	0.4	1.4	...	31.6	35.5
301	NaCl, Na ₂ B ₄ O ₇ ·10H ₂ O, trona, Na ₂ B ₂ O ₄ ·2NaCl·4H ₂ O	19.8	...	1.4	13.9	26.7	61.8
302	NaCl, Na ₂ CO ₃ ·7H ₂ O, trona, Na ₂ B ₂ O ₄ ·2NaCl·4H ₂ O	21.8	...	1.0	13.6	25.6	62.0

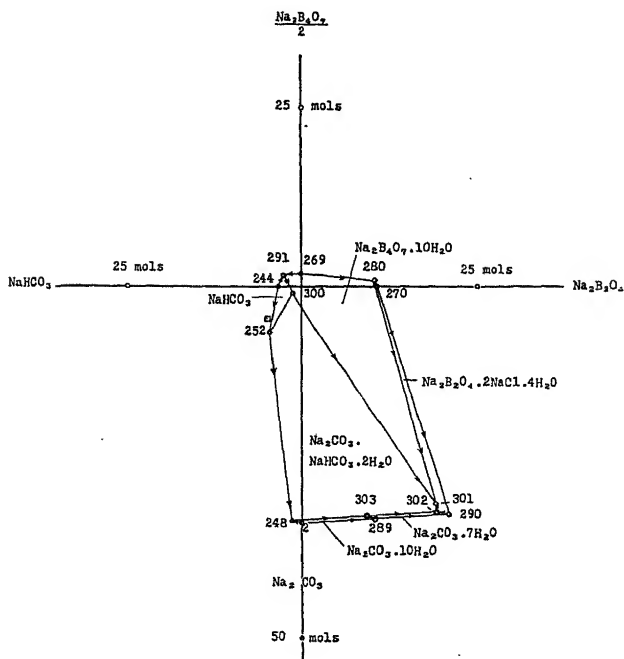
SYSTEM XII—20° C.

(Diagram 32)

Point	Solid Phases	Mols per 1,000 Mols of Water					
		Na ₂ CO ₃	NaHCO ₃	$\frac{Na_2B_4O_7}{2}$	Na ₂ B ₂ O ₄	Na ₂ Cl ₂	Total
290	NaCl, Na ₂ CO ₃ ·7H ₂ O, Na ₂ B ₂ O ₄ ·2NaCl·4H ₂ O	36.7	20.8	38.8	96.3
291	NaCl, Na ₂ B ₄ O ₇ ·10H ₂ O, NaHCO ₃	...	2.0	1.7	...	53.2	56.9
300	NaCl, Na ₂ B ₄ O ₇ ·10H ₂ O, NaHCO ₃ , trona	3.6	0.8	2.5	...	48.7	55.6
301	NaCl, Na ₂ B ₄ O ₇ ·10H ₂ O, trona, Na ₂ B ₂ O ₄ ·2NaCl·4H ₂ O	33.7	...	2.5	18.9	41.2	96.3
302	NaCl, Na ₂ CO ₃ ·7H ₂ O, trona, Na ₂ B ₂ O ₄ ·2NaCl·4H ₂ O	37.1	...	1.8	18.6	39.4	96.9

System XII - $\text{NaCl} - \text{Na}_2\text{CO}_3 - \text{NaHCO}_3 - \text{Na}_2\text{B}_4\text{O}_7 - \text{Na}_2\text{B}_2\text{O}_4 - \text{H}_2\text{O} - 20^\circ\text{C}.$

All Points Saturated with NaCl .



m - $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ Crystallization Starting Point.

302 - End Point of Crystallization.

DIAGRAM 32.

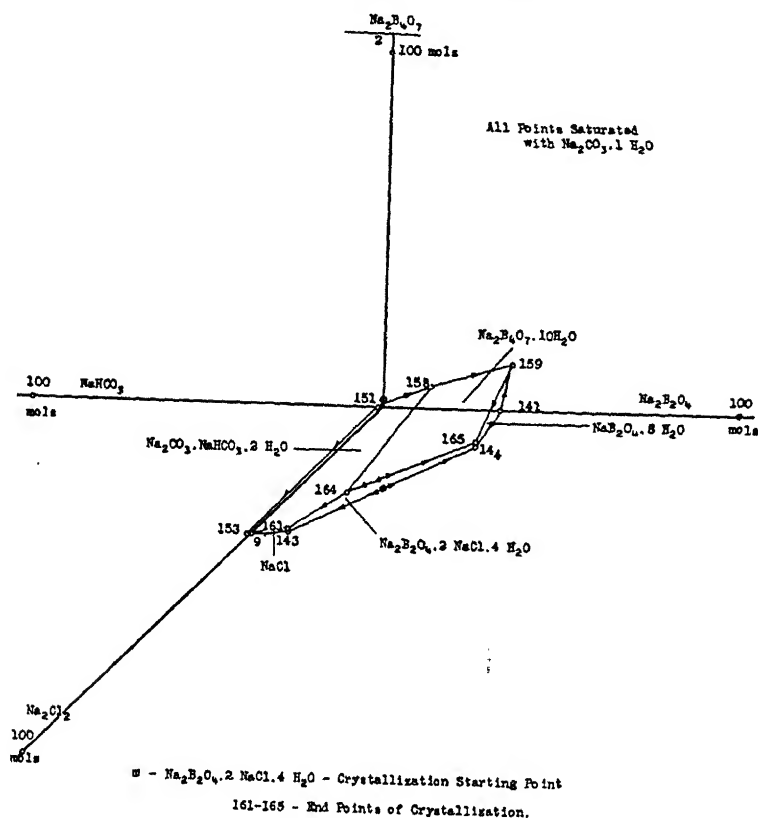
System XII - $\text{NaCl} - \text{Na}_2\text{CO}_3 - \text{NaHCO}_3 - \text{Na}_2\text{B}_4\text{O}_7 - \text{Na}_2\text{B}_2\text{O}_4 - \text{H}_2\text{O} - 35^\circ\text{C}$ 

DIAGRAM 34.

SYSTEM XII—35° C.
(Diagrams 33 and 34)

Point	Solid Phases	Mols per 1,000 Mols of Water					
		Na_2Cl_2	Na_2CO_3	NaHCO_3	$\frac{\text{Na}_2\text{B}_4\text{O}_7}{2}$	$\text{Na}_2\text{B}_2\text{O}_4$	Total
161	NaCl , $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, trona, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$	35.6	38.1	...	0.5	9.2	83.4
162	NaCl , NaHCO_3 , trona, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	50.3	8.6	2.7	5.4	...	67.0
163	NaCl , trona, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$	40.0	27.5	...	7.4	7.3	82.2
164	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, trona, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	24.0	44.7	...	6.5	14.0	89.2
165	Na_2CO_3 , $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$	9.6	41.1	...	15.2	37.1	103.0

SYSTEM XIII *

Sodium Carbonate, Potassium Carbonate, Sodium Bicarbonate,
Potassium Bicarbonate, Water

(Diagram 35)

This is a four-component system of reciprocal salt pairs, the carbonate and bicarbonate of potassium and sodium. Three double salts appear in Diagram 35 at 35° C., all of which have been previously reported; $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ or trona, $\text{K}_2\text{CO}_3 \cdot 2\text{KHCO}_3 \cdot 3\text{H}_2\text{O}$, and $\text{Na}_2\text{CO}_3 \cdot \text{K}_2\text{CO}_3$. Note the high solubility at point 171, the end point of crystallization, over 122 grams salts per 100 grams water.

SYSTEM XIII—35° C.
(Diagram 35)

Point	Solid Phases	Grams per 100 Grams of Water				
		Na_2CO_3	K_2CO_3	NaHCO_3	KHCO_3	Total
7	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	49.2	49.2
38	$\text{K}_2\text{CO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$	115.2	115.2
145	NaHCO_3	11.7	...	11.7
166	KHCO_3	40.7	40.7
151	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, trona	49.2	...	0.8	...	50.0
152	NaHCO_3 , trona	21.8	...	6.2	...	28.0
167 $3\text{H}_2\text{O}$	113.1	...	9.6	122.7
168 $3\text{H}_2\text{O}$	105.0	...	10.9	115.9
82 $3\text{H}_2\text{O}$	14.3	95.7	110.0
83	K_2CO_3	9.3	108.8	118.1
169 $3\text{H}_2\text{O}$	3.4	40.8	44.2
170 $3\text{H}_2\text{O}$
171	$\text{K}_2\text{CO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, $\text{Na}_2\text{CO}_3 \cdot \text{K}_2\text{CO}_3$, $\text{K}_2\text{CO}_3 \cdot 2\text{KHCO}_3 \cdot 3\text{H}_2\text{O}$	11.8	88.6	7.0	...	107.4
172	KHCO_3 , trona, $\text{K}_2\text{CO}_3 \cdot 2\text{KHCO}_3 \cdot 3\text{H}_2\text{O}$	4.8	112.5	5.2	...	122.5
173	KHCO_3 , NaHCO_3 , trona	6.2	81.7	12.3	...	100.2
174	KHCO_3 , NaHCO_3 , trona	3.9	51.3	17.9	...	73.1
 $3\text{H}_2\text{O}$	10.6	98.0	5.7	...	114.3

SYSTEM XIII—35° C.
(Diagram 35)

Point	Solid Phases	Mols per 1,000 Mols of Water				
		Na_2CO_3	K_2CO_3	$\text{Na}_2(\text{HCO}_3)_2$	$\text{K}_2(\text{HCO}_3)_2$	Total
7	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	83.7	83.7
38	$\text{K}_2\text{CO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$	150.0	150.0
145	NaHCO_3	12.6	...	12.6
166	KHCO_3	36.6	36.6
151	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, trona	83.6	...	0.9	...	84.5
152	NaHCO_3 , trona	37.1	...	6.7	...	43.8
167 $3\text{H}_2\text{O}$	147.3	...	8.6	155.9
168 $3\text{H}_2\text{O}$	136.8	...	9.8	146.6
82 $3\text{H}_2\text{O}$	24.2	124.6	148.8
83	$\text{K}_2\text{CO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, $\text{Na}_2\text{CO}_3 \cdot \text{K}_2\text{CO}_3$	15.8	141.8	157.6
169	NaHCO_3 , KHCO_3	3.6	36.7	40.3
170	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, trona, $\text{K}_2\text{CO}_3 \cdot 2\text{KHCO}_3 \cdot 3\text{H}_2\text{O}$	20.0	115.3	7.5	...	142.8
171	$\text{K}_2\text{CO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, $\text{Na}_2\text{CO}_3 \cdot \text{K}_2\text{CO}_3$	8.1	146.5	5.6	...	160.2
172	KHCO_3 , trona, $\text{K}_2\text{CO}_3 \cdot 2\text{KHCO}_3 \cdot 3\text{H}_2\text{O}$	10.6	106.5	13.2	...	130.3
173	KHCO_3 , NaHCO_3 , trona	6.7	66.8	19.2	...	92.7
174	Na_2CO_3	18.0	127.7	6.1	...	151.8

* Systems XIII to XXI inclusive are by Harald de Ropp working with the advice and guidance of William E. Burke.

SYSTEM XLII - $\text{Na}_2\text{CO}_3 - \text{K}_2\text{CO}_3 - \text{NaHCO}_3 - \text{KHCO}_3 - \text{H}_2\text{O}$

35°C

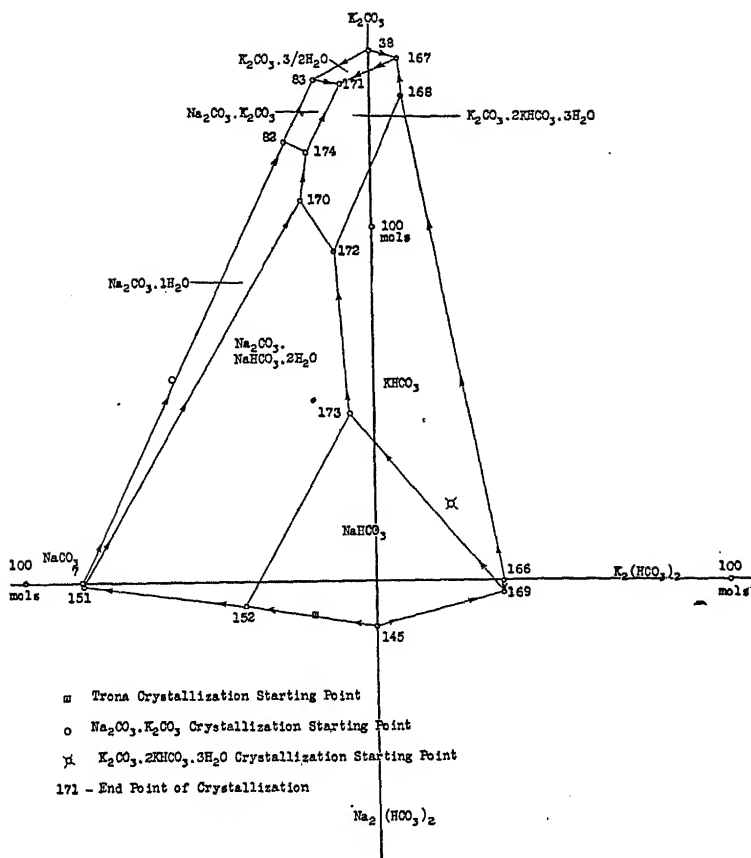


DIAGRAM 35.

SYSTEM XIV

Sodium Chloride, Potassium Chloride, Sodium Tetraborate, Potassium Tetraborate, Water

(Diagram 36)

The chloride and tetraborate of potassium and sodium also form a four-component system with reciprocal salt pairs. No double salts were found, but potassium tetraborate increases the solubility of borax, and borax increases the solubility of potassium tetraborate, so that at point 176 in Diagram 36 the solution contains more of each salt than water alone would. Potassium tetraborate appears here as the tetrahydrate. Sodium tetraborate in our equilibrium work has appeared only as the penta- or decahydrate, but a natural deposit of rasorite recently discovered about 60 miles south of Trona is apparently sodium tetraborate tetrahydrate.

SYSTEM XIV—35° C.

(Diagram 36)

Point	Solid Phases	Grams per 100 Grams of Water				
		NaCl	KCl	Na ₂ B ₄ O ₇	K ₂ B ₄ O ₇	Total
6	NaCl	36.3	36.3
37	KCl	39.0	39.0
146	Na ₂ B ₄ O ₇ ·10H ₂ O	5.3	...	5.3
175	K ₂ B ₄ O ₇ ·4H ₂ O	21.3	21.3
62	NaCl, KCl	29.8	18.4	48.2
148	NaCl, Na ₂ B ₄ O ₇ ·10H ₂ O	35.5	...	2.2	...	37.7
176	Na ₂ B ₄ O ₇ ·10H ₂ O, K ₂ B ₄ O ₇ ·4H ₂ O	6.7	24.2	30.9
177	KCl, K ₂ B ₄ O ₇ ·4H ₂ O	37.3	...	5.9	43.2
178	NaCl, KCl, Na ₂ B ₄ O ₇ ·10H ₂ O	28.2	18.7	3.4	...	50.3
179	KCl, Na ₂ B ₄ O ₇ ·10H ₂ O, K ₂ B ₄ O ₇ ·4H ₂ O...	5.4	33.2	9.9	...	48.5

SYSTEM XIV—35° C.

(Diagram 36)

Point	Solid Phases	Mols per 1,000 Mols of Water				
		Na ₂ Cl ₂	K ₂ Cl ₂	Na ₂ B ₄ O ₇	K ₂ B ₄ O ₇	Total
6	NaCl	55.8	55.8
37	KCl	47.1	47.1
146	Na ₂ B ₄ O ₇ ·10H ₂ O	4.7	...	4.7
175	K ₂ B ₄ O ₇ ·4H ₂ O	16.4	16.4
62	NaCl, KCl	45.9	22.2	68.1
148	NaCl, Na ₂ B ₄ O ₇ ·10H ₂ O	54.6	...	2.0	...	56.6
176	Na ₂ B ₄ O ₇ ·10H ₂ O, K ₂ B ₄ O ₇ ·4H ₂ O	6.0	18.6	24.6
177	NaCl, KCl, Na ₂ B ₄ O ₇ ·10H ₂ O	45.0	...	4.5	49.5
178	NaCl, KCl, Na ₂ B ₄ O ₇ ·10H ₂ O	43.5	22.6	3.0	...	69.1
179	KCl, Na ₂ B ₄ O ₇ ·10H ₂ O, K ₂ B ₄ O ₇ ·4H ₂ O...	8.3	40.0	8.9	...	57.2

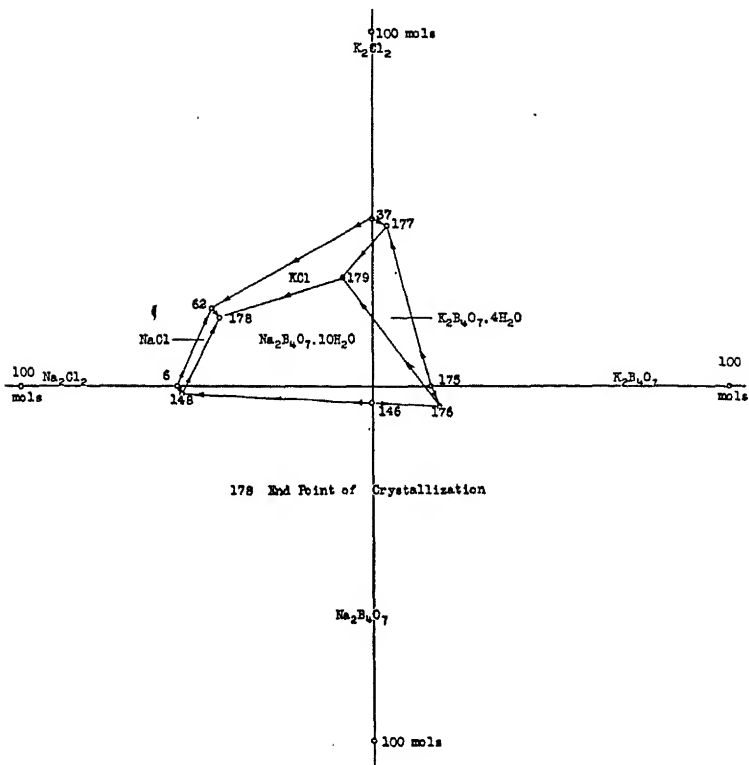
SYSTEM XIV - $\text{NaCl} - \text{KCl} - \text{Na}_2\text{B}_4\text{O}_7 - \text{K}_2\text{B}_4\text{O}_7 - \text{H}_2\text{O} - 35^\circ\text{C}$ 

DIAGRAM 36.

SYSTEM XV

Sodium Chloride, Potassium Chloride, Sodium Pentaborate, Potassium Pentaborate, Water

(Diagram 37)

The chloride and pentaborate of sodium and potassium form another four-component system of reciprocal salt pairs.

In plant practice we meet three groups of combinations between alkali and boric acid:

1. The metaborate of type $\text{Na}_2\text{O} \cdot 1\text{B}_2\text{O}_3$
2. The tetraborate of type $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$
3. The pentaborate of type $\text{Na}_2\text{O} \cdot 5\text{B}_2\text{O}_3$,

a most interesting and remarkable group of compounds often exhibiting quite unexpected behavior, but at that not so erratic as their nomen-

SYSTEM XV—35° C.

(Diagram 37)

Point	Solid Phases	Grams per 100 Grams of Water				
		NaCl	KCl	$\text{Na}_2\text{B}_{10}\text{O}_{16}$	$\text{K}_2\text{B}_{10}\text{O}_{16}$	Total
6	NaCl	36.3	36.3
37	KCl	39.0	39.0
180	$\text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$	18.8	...	18.8
181	$\text{K}_2\text{B}_{10}\text{O}_{16} \cdot 8\text{H}_2\text{O}$	5.0	5.0
62	NaCl, KCl	29.8	18.4	48.2
182	KCl, $\text{K}_2\text{B}_{10}\text{O}_{16} \cdot 8\text{H}_2\text{O}$	38.1	...	3.0	41.1
183	NaCl, $\text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$	35.1	...	7.4	...	42.5
184	$\text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$, $\text{K}_2\text{B}_{10}\text{O}_{16} \cdot 8\text{H}_2\text{O}$	17.3	1.9	19.2
185	NaCl, KCl, $\text{K}_2\text{B}_{10}\text{O}_{16} \cdot 8\text{H}_2\text{O}$	28.3	19.1	3.4	...	50.8
186	NaCl, $\text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$, $\text{K}_2\text{B}_{10}\text{O}_{16} \cdot 8\text{H}_2\text{O}$	34.5	2.1	8.2	...	44.8

SYSTEM XV—35° C.

(Diagram 37)

Point	Solid Phases	Mols per 1,000 Mols of Water				
		Na_2Cl_2	K_2Cl_2	$\text{Na}_2\text{B}_{10}\text{O}_{16}$	$\text{K}_2\text{B}_{10}\text{O}_{16}$	Total
6	NaCl	55.8	55.8
37	KCl	47.1	47.1
180	$\text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$	8.2	...	8.2
181	$\text{K}_2\text{B}_{10}\text{O}_{16} \cdot 8\text{H}_2\text{O}$	2.0	2.0
62	NaCl, KCl	45.9	22.2	68.1
182	KCl, $\text{K}_2\text{B}_{10}\text{O}_{16} \cdot 8\text{H}_2\text{O}$	46.0	...	1.2	47.2
183	NaCl, $\text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$	54.0	...	3.2	...	57.2
184	$\text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$, $\text{K}_2\text{B}_{10}\text{O}_{16} \cdot 8\text{H}_2\text{O}$	7.6	0.8	8.4
185	NaCl, KCl, $\text{K}_2\text{B}_{10}\text{O}_{16} \cdot 8\text{H}_2\text{O}$	43.6	23.1	1.5	...	68.2
186	NaCl, $\text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$, $\text{K}_2\text{B}_{10}\text{O}_{16} \cdot 8\text{H}_2\text{O}$	53.1	2.6	3.6	...	59.3

clature. Sodium pentaborate at 35° C. is over three times as soluble as borax, while potassium pentaborate has only one-fourth the solubility of $K_2B_4O_7$. At 35° sodium pentaborate appears with $10H_2O$, while the potassium salt has $8H_2O$. The pentaborates are the first products so far mentioned that are not, properly speaking, natural constituents of the brine. This system, and the next six to follow, represent conditions that could be reached only by the use of some acid. They are obviously parts of studies intended to throw some light on the conversion of borax into more acid borates or boric acid, but the reader will understand that the data given here represent only a portion of the work done, hardly adequate to derive economic conclusions regarding plant practice.

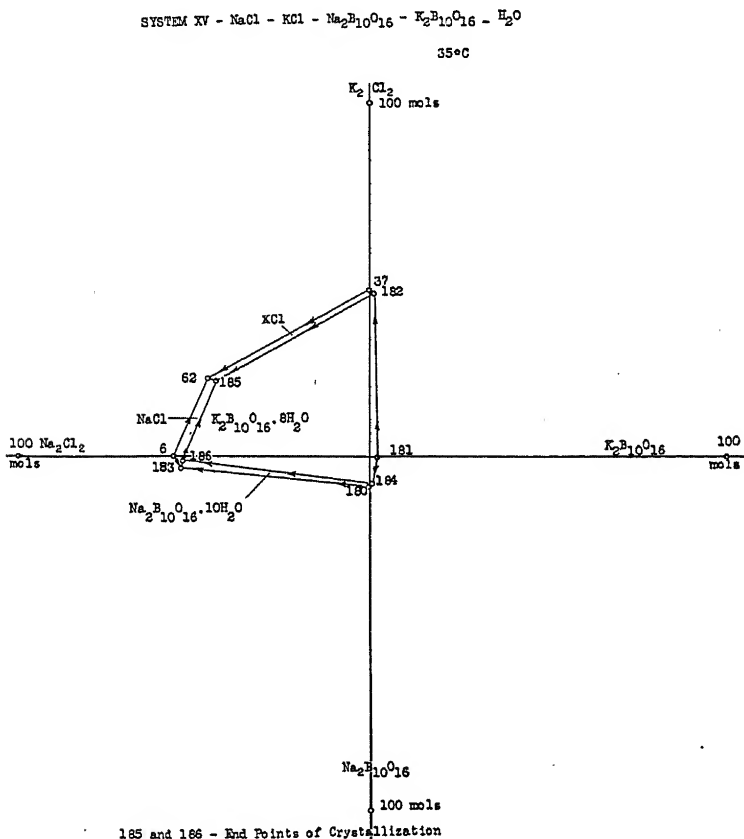


DIAGRAM 37.

SYSTEM XVI

Sodium Chloride, Sodium Sulfate, Boric Acid, Water

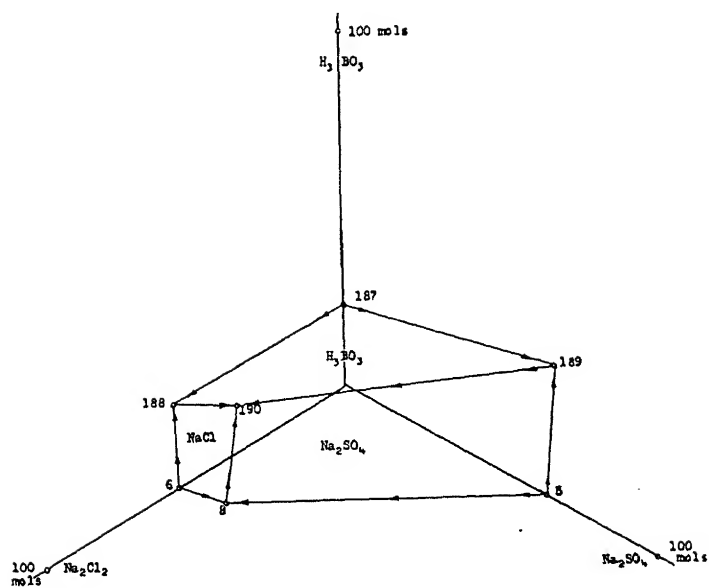
(Diagrams 38, 39)

This is a four-component system, with the three solid constituents as the only possible solid phases. The presence of Na_2SO_4 may increase the solubility of boric acid as much as 65 per cent (data for Diagram 38) and at the same time boric acid slightly increases the solubility of either sulfate or chloride. A solution saturated at 75° C. with NaCl , Na_2SO_4 and boric acid (point 194, Diagram 39) if diluted slightly can be cooled to 35° and will deposit nearly 60 per cent of its H_3BO_3 content as boric acid crystals uncontaminated with either chloride or sulfate.

SYSTEM XVI—35° C.

(Diagram 38)

Point	Solid Phases	Grams per 100 Grams of Water				Mols per 1,000 Mols of Water			
		NaCl	Na_2SO_4	H_3BO_3	Total	Na_2Cl_2	Na_2SO_4	H_3BO_3	Total
6	NaCl	36.3	36.3	55.8	55.8
5	Na_2SO_4	50.7	...	50.7	...	64.2	...	64.2
187	H_3BO_3	7.9	7.9	22.8	22.8
8	NaCl , Na_2SO_4	33.6	9.3	...	42.9	51.8	11.7	...	63.5
188	NaCl , H_3BO_3	36.8	...	8.2	45.0	56.6	...	23.9	80.5
189	Na_2SO_4 , H_3BO_3	53.0	13.1	66.1	...	67.1	38.1	105.2
190	NaCl , Na_2SO_4 , H_3BO_3	33.2	11.9	9.6	54.7	51.1	15.1	28.0	94.2

SYSTEM XVI - $\text{NaCl} - \text{Na}_2\text{SO}_4 - \text{H}_3\text{BO}_3 - \text{H}_2\text{O} - 35^\circ\text{C}$ 

190 - End Point of Crystallization.

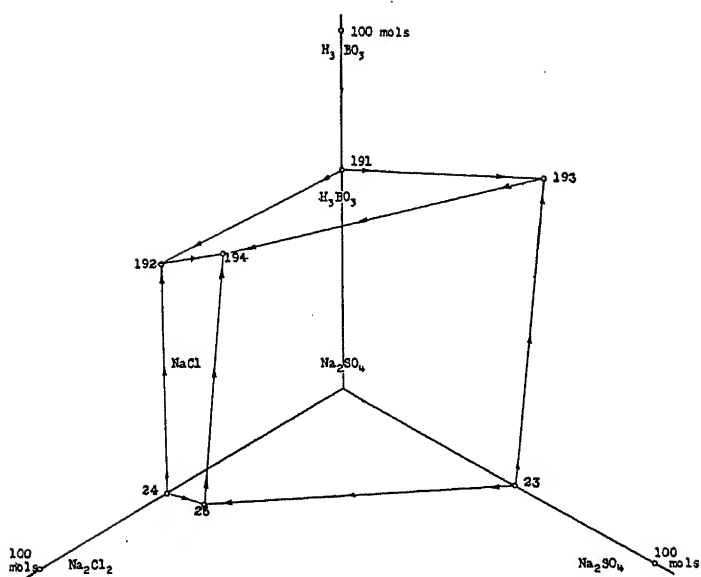
DIAGRAM 38.

SYSTEM XVI—75° C.

(Diagram 39)

Point	Solid Phases	Grams per 100 Grams of Water				Mols per 1,000 Mols of Water			
		NaCl	Na ₂ SO ₄	H ₃ BO ₃	Total	Na ₂ Cl ₂	Na ₂ SO ₄	H ₃ BO ₃	Total
24	NaCl	37.8	37.8	58.2	58.2
23	Na ₂ SO ₄	43.9	...	43.9	...	55.6	...	55.6
191	H ₃ BO ₃ *	21.1	21.1	61.2	61.2
26	NaCl, Na ₂ SO ₄	35.5	6.8	...	42.3	54.7	8.6	...	63.3
192	NaCl, H ₃ BO ₃	38.5	...	22.2	60.7	59.2	...	64.5	123.7
193	Na ₂ SO ₄ , H ₃ BO ₃	51.7	31.4	83.1	...	65.5	91.0	156.5
194	NaCl, Na ₂ SO ₄ , H ₃ BO ₃	35.5	12.4	25.0	72.9	54.6	15.7	72.6	142.9

* Probably taken from literature.

SYSTEM XVI - NaCl - Na_2SO_4 - H_3BO_3 - H_2O - 75°C 

194 - End Point of Crystallization.

DIAGRAM 39.

SYSTEM XVII

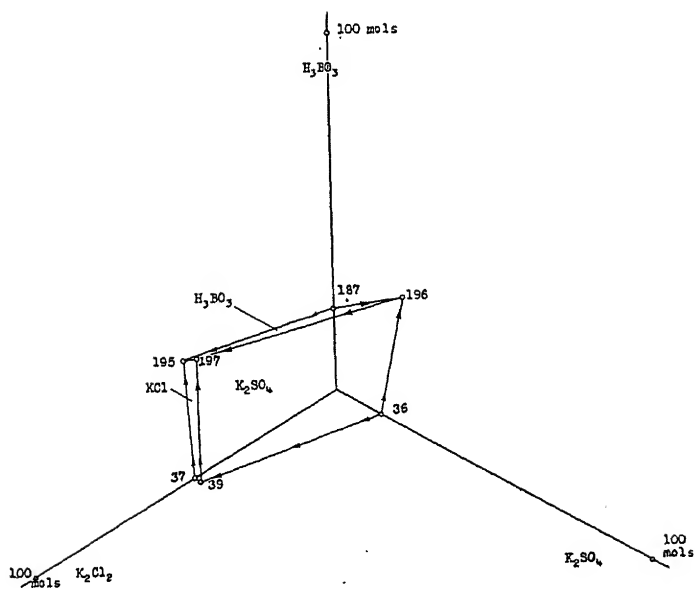
Potassium Chloride, Potassium Sulfate, Boric Acid, Water
(Diagram 40)

This is a four-component system with only three possible solid phases at 35°, much like the preceding. Note again how H_3BO_3 on one hand and K_2SO_4 or KCl on the other mutually increase solubility.

SYSTEM XVII—35° C.
(Diagram 40)

Point	Solid Phases	Grams per 100 Grams of Water				Mols per 1,000 Mols of Water			
		KCl	K_2SO_4	H_3BO_3	Total	K_2Cl_2	K_2SO_4	H_3BO_3	Total
37	KCl	39.0	39.0	47.1	47.1
36	K_2SO_4	14.1	...	14.1	...	14.5	...	14.5
187	H_3BO_3	7.9	7.9	22.8	22.8
39	KCl, K_2SO_4	38.4	1.7	...	40.1	46.4	1.7	...	48.1
195	KCl, H_3BO_3	41.0	...	11.6	52.6	49.4	...	33.6	83.0
196	K_2SO_4 , H_3BO_3	21.2	12.5	33.7	...	21.9	36.4	58.3
197	KCl, K_2SO_4 , H_3BO_3	39.9	2.8	12.1	54.8	48.2	2.9	35.1	86.2

SYSTEM XV11 - $\text{KCl} - \text{K}_2\text{SO}_4 - \text{H}_3\text{BO}_3 - \text{H}_2\text{O} - 35^\circ\text{C}$



197 - End Point of Crystallization.

DIAGRAM 40.

SYSTEM XVIII

Potassium Chloride, Potassium Tetraborate, Potassium
Pentaborate, Water

(Diagram 41)

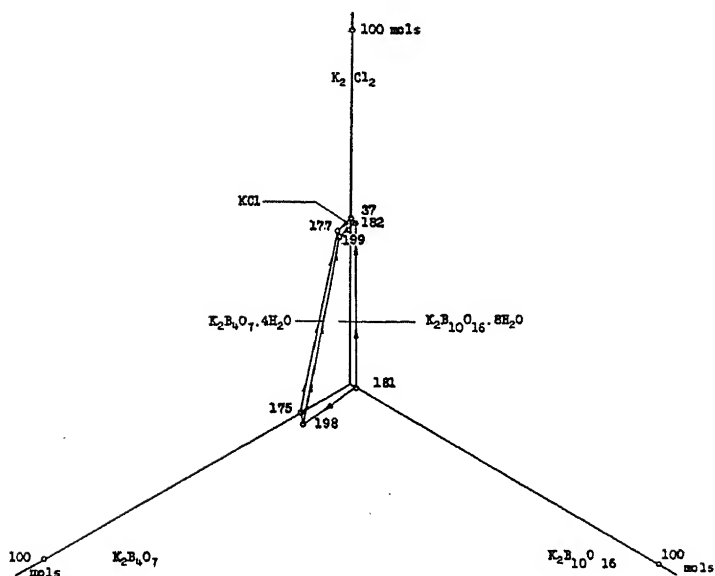
Water and the chloride, tetraborate and pentaborate of potassium form a four-component system with three possible solid phases at this temperature. By a slightly different selection of components Systems XVIII and XIX could have been presented together as one system composed of KCl , $\text{K}_2\text{B}_4\text{O}_7$, H_3BO_3 and H_2O , and this method has been adopted in Systems XX and XXI, which are quite similar, but the diagrams in the latter case are a little difficult to visualize.

SYSTEM XVIII—35° C.

(Diagram 41)

Point	Solid Phases	Grams per 100 Grams of Water				Mols per 1,000 Mols of Water			
		KCl	$\text{K}_2\text{B}_4\text{O}_7$	$\text{K}_2\text{B}_{10}\text{O}_{16}$	Total	K_2Cl_2	$\text{K}_2\text{B}_4\text{O}_7$	$\text{K}_2\text{B}_{10}\text{O}_{16}$	Total
37	KCl	39.0	39.0	47.1	47.1
175	$\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$	21.3	...	21.3	...	16.4	...	16.4
181	$\text{K}_2\text{B}_{10}\text{O}_{16} \cdot 8\text{H}_2\text{O}$	5.0	5.0	2.0	2.0
177	KCl , $\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$	37.3	5.9	...	43.2	45.0	4.5	...	49.5
182	KCl , $\text{K}_2\text{B}_{10}\text{O}_{16} \cdot 8\text{H}_2\text{O}$	38.1	...	3.0	41.1	46.0	...	1.2	47.2
198	$\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$, $\text{K}_2\text{B}_{10}\text{O}_{16} \cdot 8\text{H}_2\text{O}$	23.8	8.0	31.8	...	18.3	3.2	21.5
199	KCl , $\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$, $\text{K}_2\text{B}_{10}\text{O}_{16} \cdot 8\text{H}_2\text{O}$	36.8	6.7	3.5	47.0	44.5	5.2	1.4	51.1

SYSTEM XVIII - $\text{KCl} - \text{K}_2\text{B}_4\text{O}_7 - \text{K}_2\text{B}_{10}\text{O}_{16} - \text{H}_2\text{O} - 35^\circ\text{C}$



199 - End Point of Crystallisation.

DIAGRAM 41.

SYSTEM XIX

Potassium Chloride, Potassium Pentaborate, Boric Acid, Water
(Diagram 42)

A four-component system with three possible solid phases at this temperature. It is really a continuation of System XVIII.

SYSTEM XIX—35° C.

(Diagram 42)

Point	Solid Phases	Grams per 100 Grams of Water				Mols per 1,000 Mols of Water			
		KCl	K ₂ B ₁₀ O ₁₆	H ₃ BO ₃	Total	K ₂ Cl ₂	K ₂ B ₁₀ O ₁₆	H ₃ BO ₃	Total
37	KCl	39.0	39.0	47.1	47.1
181	K ₂ B ₁₀ O ₁₆ ·8H ₂ O	5.0	...	5.0	...	2.0	...	2.0
187	H ₃ BO ₃	7.9	7.9	22.8	22.8
182	KCl, K ₂ B ₁₀ O ₁₆ ·8H ₂ O	38.1	3.0	...	41.1	46.0	1.2	...	47.2
195	KCl, H ₃ BO ₃	41.0	...	11.6	52.6	49.4	...	33.6	83.0
200	K ₂ B ₁₀ O ₁₆ ·8H ₂ O, H ₃ BO ₃	2.4	7.1	9.5	...	1.0	20.7	21.7
201	KCl, K ₂ B ₁₀ O ₁₆ ·8H ₂ O, H ₃ BO ₃	40.7	0.3	11.0	52.0	49.2	0.1	32.0	81.3

SYSTEM XLX - $\text{KCl} - \text{K}_2\text{B}_{10}\text{O}_{16} - \text{H}_3\text{BO}_3 - \text{H}_2\text{O} - 35^\circ\text{C}$

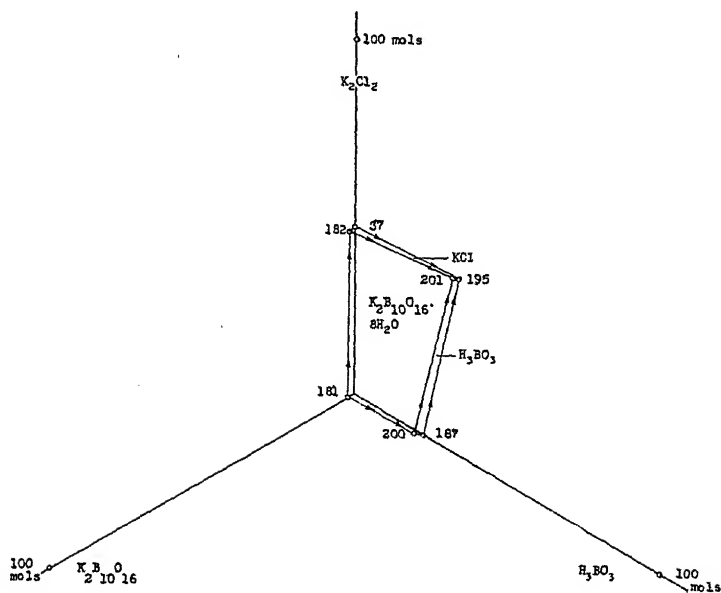


DIAGRAM 42.

SYSTEM XX

Sodium Chloride, Sodium Tetraborate, Boric Acid, Water

(Diagram 43)

This is a four-component system with four possible solid phases at this temperature, NaCl, borax, sodium pentaborate and boric acid. The diagram is rather difficult to follow because of the abnormal changes in solubility, but a little study in connection with the data sheet will probably make it clear. The H_3BO_3 field bounded by lines connecting points 188, 205, 203, 187, is entirely hidden from the observer. The pentaborate field shows two reentrant angles, 205, 183, 204 at the top and 203, 180, 202 at the bottom.

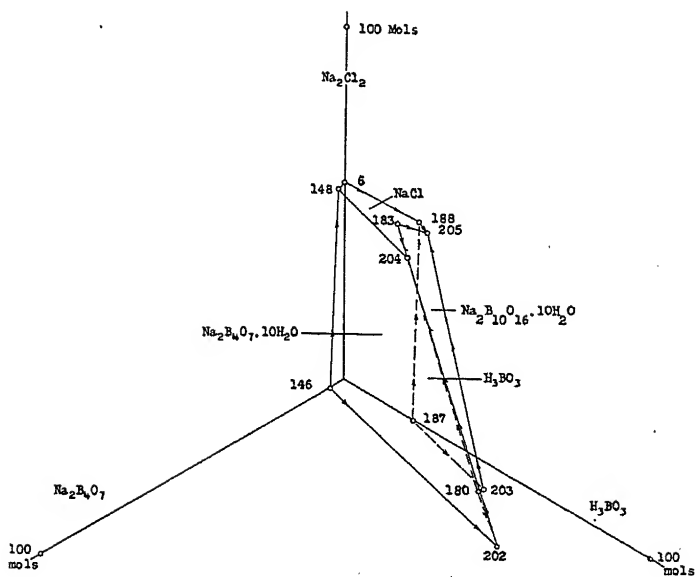
The solubility of borax at 35° C. is 4.7 mols per 1000 mols water, that of boric acid is 22.8, but a solution of both (point 202, Diagram 43) may contain 21 mols borax and 71.6 boric acid.

SYSTEM XX—35° C.

(Diagram 43)

Point	Solid Phases	Grams per 100 Grams of Water				Mols per 1,000 Mols of Water			
		NaCl	$\text{Na}_2\text{B}_4\text{O}_7$	H_3BO_3	Total	Na_2Cl_2	$\text{Na}_2\text{B}_4\text{O}_7$	H_3BO_3	Total
6	NaCl	36.3	36.3	55.8	55.8
146	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$...	5.3	...	5.3	...	4.7	...	4.7
187	H_3BO_3	7.9	7.9	22.8	22.8
148	$\text{NaCl}, \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	35.5	2.2	...	37.7	54.6	2.0	...	56.6
188	$\text{NaCl}, \text{H}_3\text{BO}_3$	36.8	...	8.2	45.0	56.6	...	23.9	80.5
202	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}, \text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$...	23.6	24.7	48.3	...	21.0	71.6	92.6
203	$\text{H}_3\text{BO}_3, \text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$...	8.4	18.4	26.8	...	7.5	53.5	61.0
180	$\text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$...	9.9	18.3	28.2	...	8.9	53.1	62.0
183	$\text{NaCl}, \text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$	36.1	3.7	6.9	46.7	55.6	3.3	20.0	78.9
204	$\text{NaCl}, \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}, \text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$	34.6	10.1	10.0	54.7	53.3	9.0	29.0	91.3
205	$\text{NaCl}, \text{H}_3\text{BO}_3, \text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$	36.3	1.2	9.4	46.9	55.8	1.0	27.4	84.2

SYSTEM XX - NaCl - $\text{Na}_2\text{B}_4\text{O}_7$ - H_3BO_3 - H_2O - 35°C



204 - 205 - End Points of Crystallization.

DIAGRAM 43.

SYSTEM XXI

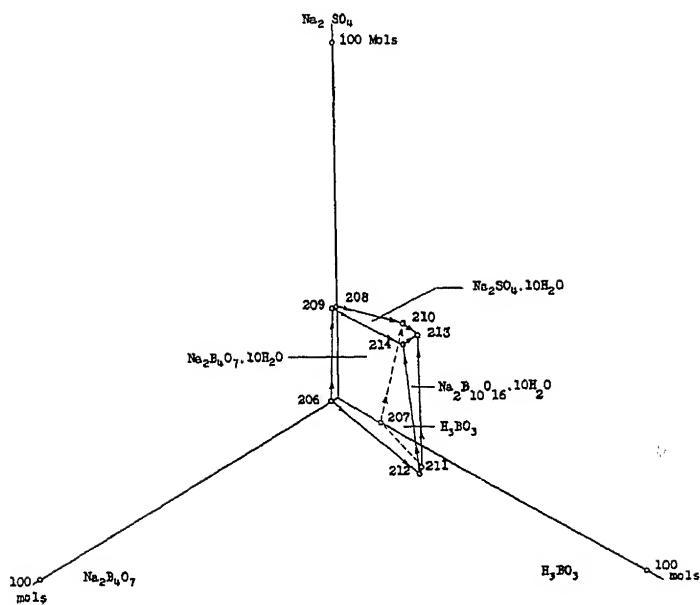
Sodium Sulfate, Sodium Tetraborate, Boric Acid, Water
(Diagrams 44, 45, 46, 47)

A four-component system similar to System XX, or to Systems XVIII and XIX combined. It will be obvious to anyone familiar with such matters that these four diagrams represent the cerebrations of a research chemist feeling his way toward a process, probably cyclic, for the manufacture of boric acid from borax and H_2SO_4 . Some bright student may wish to give his brain a little exercise by determining just what the cycle is, whether it is feasible and what structural materials he would use for his equipment.

SYSTEM XXI—20.5° C.
(Diagram 44)

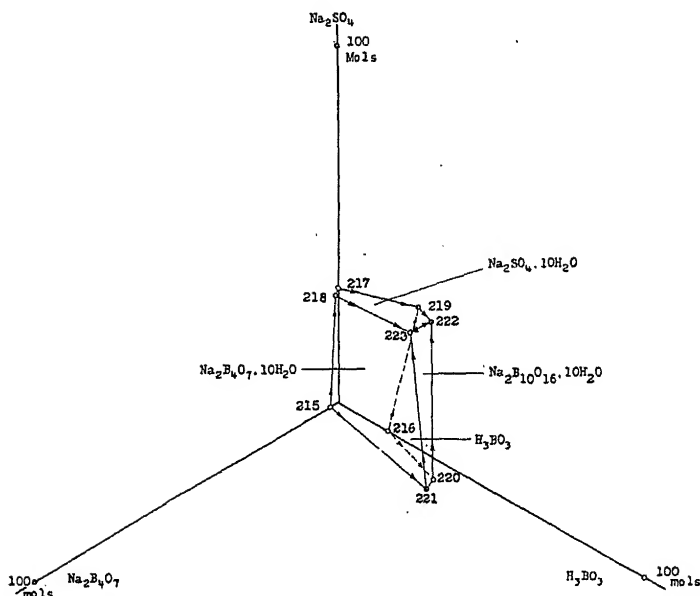
Point	Solid Phases	Grams per 100 Grams of Water				Mols per 1,000 Mols of Water			
		H_3BO_3	$\text{Na}_2\text{B}_4\text{O}_7$	Na_2SO_4	Total	H_3BO_3	$\text{Na}_2\text{B}_4\text{O}_7$	Na_2SO_4	Total
206	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	2.5	...	2.5	...	2.2	...	2.2
207	H_3BO_3	4.9	4.9	14.3	14.3
208	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	20.2	20.2	25.7	25.7
209	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	1.2	20.0	21.2	...	1.0	25.4	26.4
210	H_3BO_3 , $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	7.6	...	25.3	32.9	22.1	...	32.0	54.1
211	H_3BO_3 , $\text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$...	11.5	5.8	...	17.3	33.3	5.2	...	38.5
212	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$	12.0	8.7	...	20.7	34.8	7.7	...	42.5
213	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, H_3BO_3 , $\text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$	9.8	1.9	25.8	37.5	28.3	1.7	32.6	62.6
214	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$	8.8	4.7	23.6	37.1	25.5	4.2	29.9	59.6

SYSTEM XXI - Na_2SO_4 - $\text{Na}_2\text{B}_4\text{O}_7$ - H_3BO_3 - H_2O - 20.5°C



214 - End Point of Crystallization.

DIAGRAM 44.

SYSTEM XXI - Na_2SO_4 - $\text{Na}_2\text{B}_4\text{O}_7$ - H_3BO_3 - H_2O - 23.5°C 

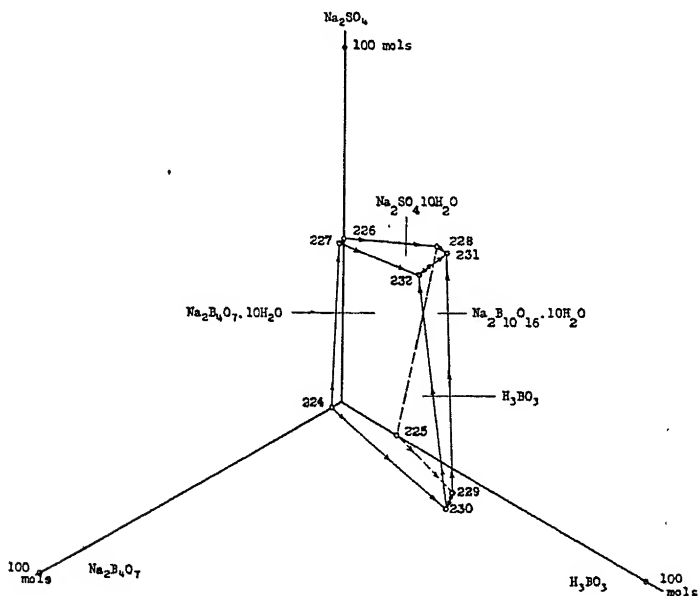
222 and 223 - End Points of Crystallization.

DIAGRAM 45.

SYSTEM XXI— 23.5°C .

(Diagram 45)

Point	Solid Phases	Grams per 100 Grams of Water				Mols per 1,000 Mols of Water			
		H_3BO_3	$\text{Na}_2\text{B}_4\text{O}_7$	Na_2SO_4	Total	H_3BO_3	$\text{Na}_2\text{B}_4\text{O}_7$	Na_2SO_4	Total
215	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$...	2.9	...	2.9	...	2.6	...	2.6
216	H_3BO_3	5.5	5.5	16.0	16.0
217	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	25.2	25.2	32.0	32.0
218	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$...	1.4	23.7	25.1	...	1.2	30.1	31.3
219	H_3BO_3	8.9	...	31.2	40.1	25.9	...	39.5	65.4
220	H_3BO_3	12.6	6.2	...	18.8	36.7	5.6	...	42.3
221	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	13.2	10.4	...	23.6	38.4	9.3	...	47.7
222	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	10.9	1.9	31.3	44.1	31.7	1.7	39.6	73.0
223	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	9.6	5.4	28.3	43.3	27.8	4.8	35.9	68.5

SYSTEM XXI - Na_2SO_4 - $\text{Na}_2\text{B}_4\text{O}_7$ - H_3BO_3 - H_2O ; 28.5°C

231 and 232 - End Points of Crystallization.

DIAGRAM 46.

SYSTEM XXI—28.5° C.

(Diagram 46)

Point	Solid Phases	Grams per 100 Grams of Water				Mols per 1,000 Mols of Water			
		H_3BO_3	$\text{Na}_2\text{B}_4\text{O}_7$	Na_2SO_4	Total	H_3BO_3	$\text{Na}_2\text{B}_4\text{O}_7$	Na_2SO_4	Total
224	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	3.7	...	3.7	...	3.3	...	3.3
225	H_3BO_3	6.3	6.3	18.4	18.4
226	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	36.5	36.5	46.2	46.2
227	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	1.7	36.1	37.8	...	1.5	45.8	47.3
228	H_3BO_3	10.6	...	47.3	57.9	30.9	...	59.9	90.8
229	H_3BO_3	14.9	7.0	...	21.9	43.2	6.3	...	49.5
230	$\text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$	16.2	13.4	...	29.6	47.0	12.0	...	59.0
231	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	12.1	1.7	47.8	61.6	35.3	1.5	60.6	97.4
232	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	10.6	7.1	43.1	60.8	30.7	6.4	54.6	91.7

SYSTEM XXII *

Sodium Bicarbonate, Sodium Carbonate, Sodium Sulfate, Water
(Diagram 48)

After this digression regarding acid borates and boric acid we now revert to the constituents actually present in lake brine. The five-component system water and the chloride, sulfate, carbonate and bicarbonate of soda contains and is limited by four four-component systems. The first one, NaCl , Na_2SO_4 , Na_2CO_3 , H_2O , was studied in System I. The second one, NaCl , Na_2CO_3 , NaHCO_3 , H_2O , will be found as System IX. The third one, NaHCO_3 , Na_2CO_3 , Na_2SO_4 , H_2O , to be discussed now differs from System IX only by having sulfate instead of chloride. The only surprising feature of Diagram 48 is the entire absence of double salts; neither trona nor burkeite appears. Trona is not in equilibrium with a solution of its constituents at 20°C . but chloride stabilizes it (see Diagram 27) and we might expect sulfate to do so. It is not so surprising to find that chloride stabilizes burkeite (Diagram 1) but bicarbonate does not. In Diagram 48 we find only the three single salts, two of them hydrated.

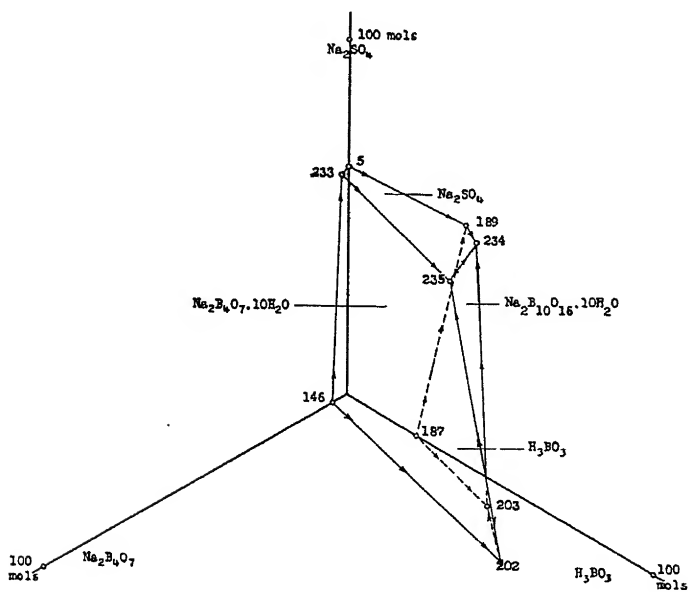
SYSTEM XXI— 35°C .

(Diagram 47)

Point	Solid Phases	Grams per 100 Grams of Water				Mols per 1,000 Mols of Water			
		H_3BO_3	$\text{Na}_2\text{B}_4\text{O}_7$	Na_2SO_4	Total	H_3BO_3	$\text{Na}_2\text{B}_4\text{O}_7$	Na_2SO_4	Total
146	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	5.3	...	5.3	...	4.7	...	4.7
187	H_3BO_3	7.9	7.9	22.8	22.8
5	Na_2SO_4	50.7	50.7	64.2	64.2
233	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, Na_2SO_4	2.7	49.7	52.4	...	2.4	62.9	65.3
189	13.1	...	53.0	66.1	38.1	...	67.1	105.2
203	18.4	8.4	...	26.8	53.5	7.5	...	61.0
202
234	Na_2SO_4 , $\text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$	24.7	23.6	...	48.3	71.6	21.0	...	92.6
	Na_2SO_4 , H_3BO_3 , $\text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$	14.9	2.3	52.1	69.3	43.2	2.1	66.0	111.3
235	Na_2SO_4 , $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$	15.2	12.4	47.0	74.6	44.0	11.1	59.6	114.7

* Systems XXII to XXIV inclusive are by W. A. Gale working under the direction of William E. Burke.

SYSTEM XXI - Na_2SO_4 - $\text{Na}_2\text{B}_4\text{O}_7$ - H_3BO_3 - H_2O - 35°C



234 and 235 - End Points of Crystallization.

DIAGRAM 47.

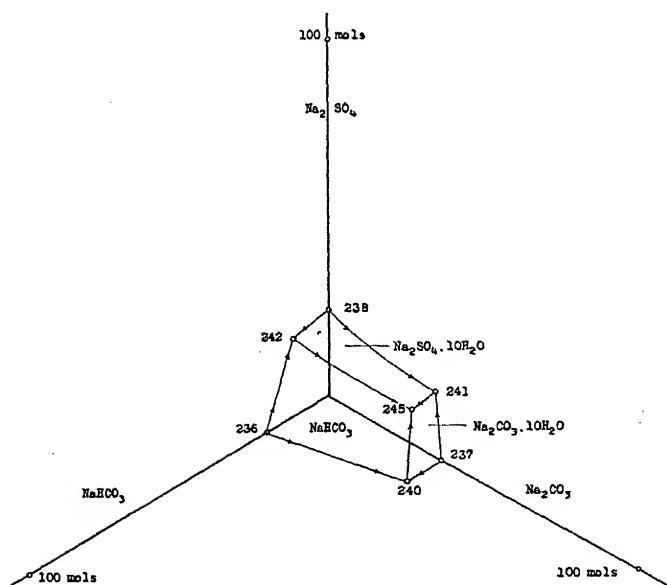
SYSTEM XXII—20° C.

(Diagram 48)

Point	Solid Phases	Grams per 100 Grams of Water				Mols per 1,000 Mols of Water			
		NaHCO ₃	Na ₂ CO ₃	Na ₂ SO ₄	Total	NaHCO ₃	Na ₂ CO ₃	Na ₂ SO ₄	Total
236	NaHCO ₃	9.6	9.6	20.6	20.6
237	Na ₂ CO ₃ ·10H ₂ O	21.5	...	21.5	...	36.5	...	36.5
238	Na ₂ SO ₄ ·10H ₂ O	19.5	19.5	24.7	24.7
* 240	NaHCO ₃ , Na ₂ CO ₃ ·10H ₂ O	5.1	21.6	...	26.7	10.9	36.7	...	47.6
* ...	NaHCO ₃	7.5	7.2	...	14.7	16.1	12.2	...	28.3
242	NaHCO ₃ , Na ₂ SO ₄ ·10H ₂ O	5.4	...	17.1	22.5	11.6	...	21.7	33.3
...	Na ₂ SO ₄ ·10H ₂ O	6.9	15.8	22.7	...	11.7	20.0	31.7
241	Na ₂ CO ₃ ·10H ₂ O	20.1	14.9	35.0	...	34.2	18.9	53.1
...	Na ₂ CO ₃ ·10H ₂ O	20.3	12.5	32.8	...	34.5	15.8	50.3
245	Na ₂ CO ₃ ·10H ₂ O, NaHCO ₃	3.9	20.6	14.7	39.2	8.4	35.0	18.6	62.0
...	Na ₂ CO ₃ ·10H ₂ O	4.8	20.8	8.1	33.7	10.3	35.4	10.3	56.0
...	Na ₂ CO ₃ ·10H ₂ O	4.5	9.7	15.5	29.7	9.7	16.5	19.6	45.8

* Points taken from Freeth, *Trans. Royal Soc.* 233A, 35 (1922).

SYSTEM XC11; $\text{NaHCO}_3 - \text{Na}_2\text{CO}_3 - \text{Na}_2\text{SO}_4 - \text{H}_2\text{O}$; 20°C .



245 - End Point of Crystallization.

DIAGRAM 48.

SYSTEM XXIII

Sodium Bicarbonate, Sodium Sulfate, Sodium Chloride, Water
(Diagram 49)

This is a four-component system with three single salts in the solid phases. The sulfate occurs both as the hydrate and anhydrous, depending on the chloride concentration. The very low solubility of bicarbonate in saturated chloride solutions is of practical importance. There are no features in Diagram 49 requiring especial notice.

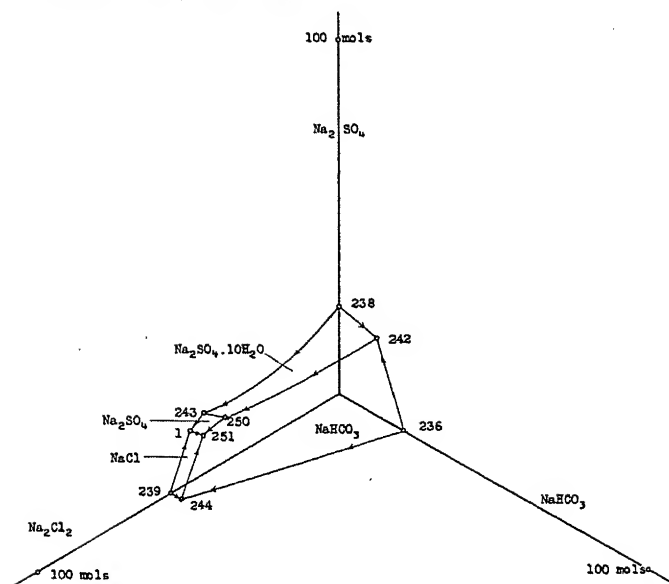
SYSTEM XXIII—20° C.

(Diagram 49)

Point	Solid Phases	Grams per 100 Grams of Water				Mols per 1,000 Mols of Water			
		NaHCO ₃	Na ₂ SO ₄	NaCl	Total	NaHCO ₃	Na ₂ SO ₄	Na ₂ Cl ₂	Total
236	NaHCO ₃	9.6	9.6	20.6	20.6
238	Na ₂ SO ₄ ·10H ₂ O	19.5	...	19.5	...	24.7	...	24.7
239	NaCl	36.0	36.0	55.5	55.5
242	NaHCO ₃ , Na ₂ SO ₄ ·10H ₂ O	5.4	17.1	...	22.5	11.6	21.7	...	33.3
...	Na ₂ SO ₄ ·10H ₂ O	12.5	11.8	24.3	...	15.8	18.2	34.0
...	Na ₂ SO ₄ ·10H ₂ O	11.7	20.4	32.1	...	14.8	31.4	36.2
...	Na ₂ SO ₄ ·10H ₂ O	12.1	26.2	38.3	...	15.3	40.4	55.7
243	Na ₂ SO ₄ ·10H ₂ O, Na ₂ SO ₄	13.0	29.0	42.0	...	16.5	44.7	61.2
1	Na ₂ SO ₄ , NaCl	11.0	31.8	42.8	...	13.9	49.0	62.9
*244	NaHCO ₃ , NaCl	1.4	...	35.8	37.2	3.0	...	55.2	58.2
250	Na ₂ SO ₄ ·10H ₂ O, Na ₂ SO ₄
...	Na ₂ SO ₄ ·10H ₂ O, NaHCO ₃	2.1	13.2	27.8	43.1	4.5	16.7	42.8	64.0
...	Na ₂ SO ₄ ·10H ₂ O, NaHCO ₃	2.0	12.5	25.8	40.3	4.3	15.8	39.7	59.8
251	Na ₂ SO ₄ , NaHCO ₃ , NaCl	1.7	10.8	31.4	43.9	3.6	13.7	48.4	65.7

* Points taken from Freeth, *Trans. Royal Soc.* 233A, 35 (1922).

SYSTEM XLIII: $\text{NaHCO}_3 - \text{Na}_2\text{SO}_4 - \text{NaCl} - \text{H}_2\text{O}$; 20°C .



251 - End Point of Crystallization.

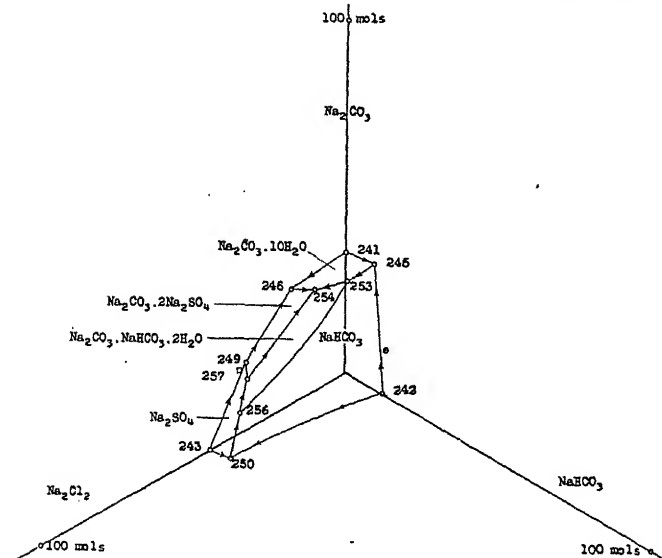
DIAGRAM 49.

SYSTEM XXIV

Sodium Bicarbonate, Sodium Carbonate, Sodium Sulfate, Sodium Chloride, Water

(Diagrams 50, 51)

This is a five-component system of water and the carbonate, bicarbonate, sulfate and chloride of sodium. We have discussed the four four-component systems leading to it in numbers I, IX, XXII and XXIII. Diagram 50 shows all points saturated with NaCl. Both of the double salts, trona and burkeite, appear at 20° C. on account of saturation with NaCl; for the same reason Na_2SO_4 occurs only as the anhydrous salt. Diagram 51 shows all points saturated with $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, consequently in this diagram NaCl cannot appear as the solid phase.

SYSTEM XXIV; $\text{NaHCO}_3 - \text{Na}_2\text{CO}_3 - \text{Na}_2\text{SO}_4 - \text{NaCl} - \text{H}_2\text{O}; 20^\circ\text{C}.$ All points saturated with $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ □ - $\text{Na}_2\text{CO}_3 \cdot 2 \text{Na}_2\text{SO}_4$, Crystallization Starting Point.○ - $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$, Crystallization Starting Point.

254 - End Point of Crystallization.

DIAGRAM 51.

SYSTEM XXIV— $20^\circ\text{C}.$

(Diagrams 50 and 51)

Point	Solid Phases	Mols per 1,000 Mols of Water				
		NaHCO_3	Na_2CO_3	Na_2Cl_2	Na_2SO_4	Total
253	$\text{NaHCO}_3, \text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}, \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}, \text{trona}$	7.7	33.1	7.2	17.7	65.7
256	$\text{NaHCO}_3, \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}, \text{Na}_2\text{SO}_4, \text{trona}$	3.6	9.0	38.8	17.5	68.9
...	$\text{NaHCO}_3, \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}, \text{trona}$	5.6	21.1	15.1	17.2	59.0
...	$\text{NaHCO}_3, \text{Na}_2\text{SO}_4, \text{trona}$	3.2	7.8	43.6	14.3	68.9
258	$\text{NaHCO}_3, \text{Na}_2\text{SO}_4, \text{NaCl}, \text{trona}$	3.2	7.3	45.9	13.2	69.6
254	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}, \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}, \text{burkeite}, \text{trona}$	3.4	32.3	14.2	17.4	67.3
255	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}, \text{NaCl}, \text{burkeite}, \text{trona}$	1.3	36.2	35.9	6.8	80.2
257	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}, \text{Na}_2\text{SO}_4, \text{burkeite}, \text{trona}$	2.1	16.1	34.4	17.4	70.0
...	$\text{NaCl}, \text{Na}_2\text{SO}_4, \text{trona}$	2.8	7.8	46.8	13.2	70.6
259	$\text{NaCl}, \text{Na}_2\text{SO}_4, \text{burkeite}, \text{trona}$	1.5	14.8	42.7	12.7	71.7

SYSTEM XXV *

Trisodium Phosphate, Disodium Phosphate, Sodium Chloride, Water
(Diagram 52)

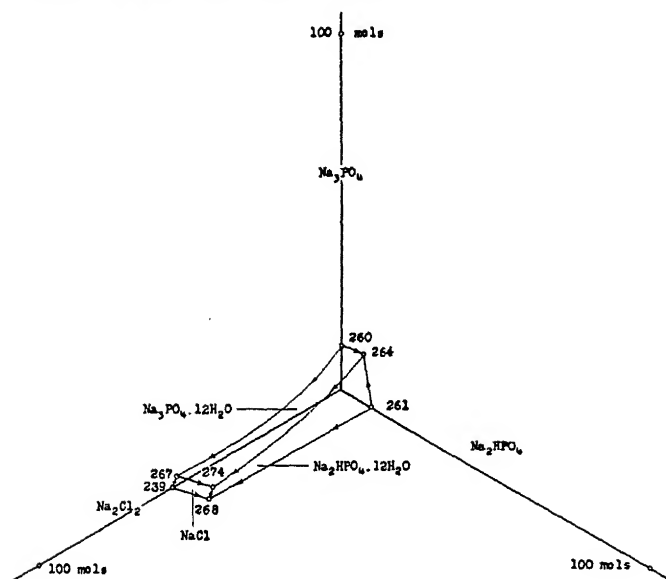
Trisodium and disodium phosphate, sodium chloride and water compose a four-component system. Phosphates may be regarded as minor constituents of the Searles Lake brine, but in plant concentration they took on major importance and it became necessary to study them. The only part of the study given here is that at 20° C.

SYSTEM XXV—20° C.
(Diagram 52)

Point	Solid Phases	Grams per 100 Grams of Water				Mols per 1,000 Mols of Water			
		Na ₃ PO ₄	Na ₂ HPO ₄	NaCl	Total	Na ₃ PO ₄	Na ₂ HPO ₄	Na ₂ Cl ₂	Total
260	Na ₃ PO ₄ ·12H ₂ O	11.45	11.45	12.57	12.57
261	Na ₂ HPO ₄ ·12H ₂ O	7.7	...	7.7	...	9.75	...	9.75
239	NaCl	36.0	36.0	55.5	55.5
...	Na ₃ PO ₄ ·12H ₂ O	3.1	...	11.6	14.7	3.4	...	17.9	21.3
...	Na ₃ PO ₄ ·12H ₂ O	11.9	1.6	...	13.5	13.1	2.0	...	15.1
...	Na ₂ HPO ₄ ·12H ₂ O	1.8	6.4	...	8.2	1.5	8.2	...	9.7
264	Na ₃ PO ₄ ·12H ₂ O, Na ₂ HPO ₄ ·12H ₂ O	12.3	5.0	...	17.3	13.5	6.3	...	19.8
267	Na ₃ PO ₄ ·12H ₂ O, NaCl	1.9	...	35.0	36.9	2.1	...	54.0	56.1
268	Na ₂ HPO ₄ ·12H ₂ O, NaCl	7.0	33.8	40.8	...	8.9	52.2	61.1
...	Na ₃ PO ₄ ·12H ₂ O, NaCl	2.1	3.4	33.5	39.0	2.3	4.3	51.6	58.2
...	Na ₃ PO ₄ ·12H ₂ O, Na ₂ HPO ₄ ·12H ₂ O	2.9	3.7	12.8	19.4	3.2	4.7	19.7	27.6
274	Na ₃ PO ₄ ·12H ₂ O, Na ₂ HPO ₄ ·12H ₂ O, NaCl	2.1	7.2	33.2	42.5	2.3	9.1	51.2	62.6

* Systems XXV, XXVI, XXVII, XXVIII, XXIX are by W. A. Gale and C. F. Ritchie working under the direction of W. E. Burke.

SYSTEM XXV; $\text{Na}_3\text{PO}_4 - \text{Na}_2\text{HPO}_4 - \text{NaCl} - \text{H}_2\text{O}$; 20°C .



274 - End Point of Crystallization.

DIAGRAM 52.

SYSTEM XXVI

Disodium Phosphate, Sodium Tetraborate, Sodium Chloride, Water
(Diagram 53)

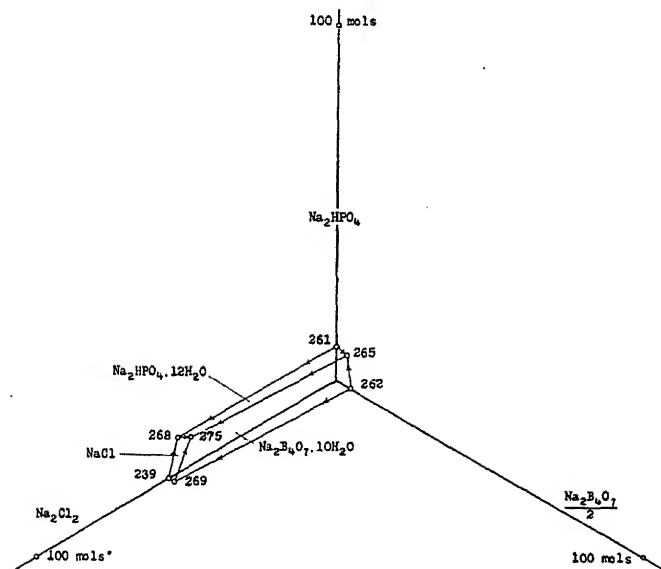
This is a four-component system. Diagram 53 shows no notable features unless it be that the phosphate is more soluble at point 275, saturated with both chloride and borax, than it is at point 261 in water alone.

SYSTEM XXVI—20° C.

(Diagram 53)

Point	Solid Phases	Grams per 100 Grams of Water				Mols per 1,000 Mols of Water			
		Na ₂ HPO ₄	Na ₂ B ₄ O ₇	NaCl	Total	Na ₂ HPO ₄	$\frac{\text{Na}_2\text{B}_4\text{O}_7}{2}$	Na ₂ Cl ₂	Total
261	Na ₂ HPO ₄ ·12H ₂ O	7.7	7.7	9.75	9.75
262	Na ₂ B ₄ O ₇ ·10H ₂ O	...	2.5	...	2.5	...	4.46	...	4.46
239	NaCl	36.0	36.0	55.5	55.5
...	Na ₂ B ₄ O ₇ ·10H ₂ O	2.6	2.0	...	4.6	3.3	3.6	...	6.9
265	Na ₂ HPO ₄ ·12H ₂ O	6.7	1.5	...	8.2	8.5	2.6	...	11.1
268	Na ₂ B ₄ O ₇ ·10H ₂ O	7.0	...	33.8	40.8	8.9	...	52.2	61.1
269	NaCl	...	0.85	36.0	36.85	...	1.5	55.5	57.0
...	Na ₂ HPO ₄ ·12H ₂ O	0.7	0.8	35.7	37.2	0.9	1.4	55.0	57.3
...	Na ₂ B ₄ O ₇ ·10H ₂ O	2.7	0.8	34.8	38.3	3.5	1.4	53.6	58.5
...	NaCl	7.2	1.0	33.3	41.5	9.1	1.8	51.3	62.2
275	Na ₂ HPO ₄ ·12H ₂ O	7.8	1.0	32.5	41.3	10.0	1.8	50.1	61.9

SYSTEM XXVI: Na_2HPO_4 - $\text{Na}_2\text{B}_4\text{O}_7$ - NaCl - H_2O ; 20°C .



275 - End Point of Crystallization.

DIAGRAM 53.

SYSTEM XXVII

Trisodium Phosphate, Sodium Metaborate, Sodium Chloride, Water
(Diagram 54)

Trisodium phosphate, sodium metaborate, sodium chloride, and water form a four-component system with five solid phases at this temperature, of which two are new double salts. One of these, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$, has been discussed previously under Systems VII, X and XII. The other, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$, appears here for the first time. A glance at Diagram 54 and at the data sheets shows the wide range over which the double phosphate metaborate is precipitated; only 0.2 gram per 100 grams water of metaborate in a strong solution of the phosphate, or only 0.03 gram trisodium phosphate in a strong solution of metaborate is needed for equilibrium with the double salt.

SYSTEM XXVII—20° C.

(Diagram 54)

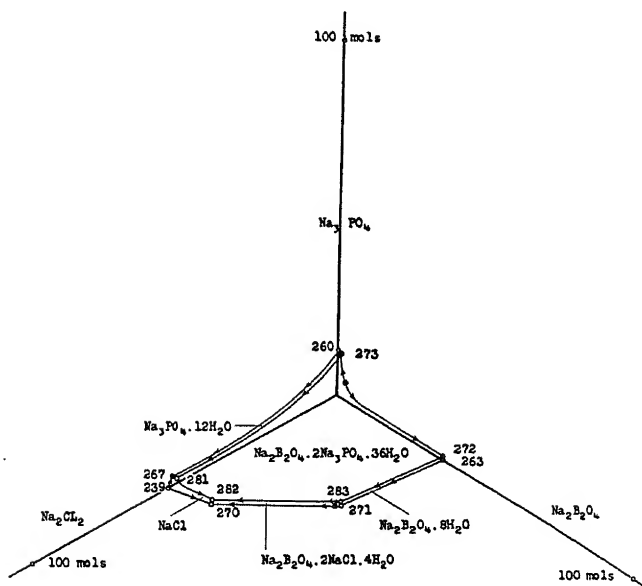
Point	Solid Phases	Grams per 100 Grams of Water			
		Na_3PO_4	$\text{Na}_2\text{B}_2\text{O}_4$	NaCl	Total
260	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	11.45	11.45
263	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$...	25.75	...	25.75
239	NaCl	36.0	36.0
273	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$	11.2	1.17	...	11.4
272	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$	2.9	0.2	...	4.07
271	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$	0.03	25.5	...	25.53
270	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$, NaCl	...	23.0	19.2	42.2
267	H_2O , NaCl	...	8.0	33.3	41.3
283	NaCl	1.9	...	35.0	36.9
282	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$	0.2	23.0	19.2	42.22
...	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$, H_2O , NaCl	0.15	8.0	33.0	41.15
...	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$, NaCl	1.5	0.6	35.0	37.1
281	NaCl , $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$	2.0	0.4	35.0	37.4

SYSTEM XXVII—20° C.

(Diagram 54)

Point	Solid Phases	Mols per 1,000 Mols of Water			
		Na_3PO_4	$\text{Na}_2\text{B}_2\text{O}_4$	Na_2Cl_2	Total
260	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	12.57	12.57
263	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$...	35.14	...	35.14
239	NaCl	55.5	55.5
273	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$	12.3	0.2	...	12.5
272	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$	3.2	1.6	...	4.8
271	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$	0.04	34.8	...	34.84
270	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$, NaCl	...	31.4	29.6	61.0
267	H_2O , NaCl	...	10.9	51.3	62.2
283	NaCl	2.1	...	54.0	56.1
282	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$, $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$	0.02	31.4	29.6	61.02
...	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$, H_2O , NaCl	0.16	10.9	50.9	61.96
...	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$, NaCl	1.6	0.8	53.9	56.3
281	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, NaCl , $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$	2.2	0.6	53.9	56.7

SYSTEM XXVII: $\text{Na}_3\text{PO}_4 - \text{Na}_2\text{B}_2\text{O}_4 - \text{NaCl} - \text{H}_2\text{O}$; 20°C .



- - $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$, Crystallization Starting Point.
 - - $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$, Crystallization Starting Point.
- 282 and 283 - End Points of Crystallisation.

DIAGRAM 54.

SYSTEM XXVIII

Trisodium Phosphate, Disodium Phosphate, Sodium Tetraborate,
Sodium Metaborate, Water (Diagram 55)
This is a four-component system of reciprocal salt pairs.

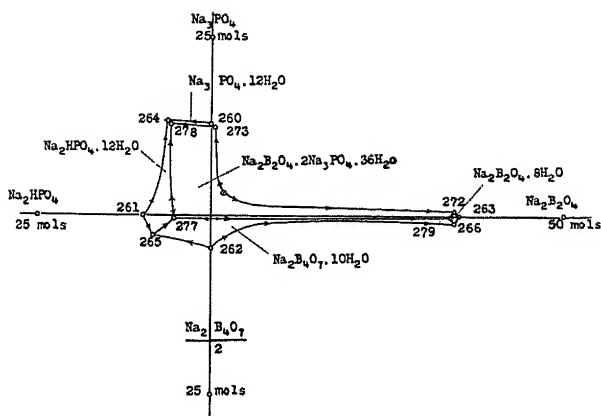
SYSTEM XXVIII—20° C.
(Diagram 55)

Point	Solid Phases	Grams per 100 Grams of Water				
		Na_3PO_4	Na_2HPO_4	$\text{Na}_2\text{B}_4\text{O}_7$	$\text{Na}_2\text{B}_2\text{O}_4$	Total
260	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	11.45	11.45
261	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$...	7.7	7.7
262	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	2.5	...	2.5
263	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 8\text{H}_2\text{O}$	25.75	25.75
264	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}, \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	12.3	5.0	17.3
...	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	11.9	1.6	13.5
...	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	1.8	6.4	8.2
265	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}, \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$...	6.7	1.5	...	8.2
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$...	2.6	2.0	...	4.6
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	1.95	0.5	2.45
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	0.5	4.9	5.4
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	0.4	11.3	11.7
266	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}, \text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$	0.5	25.1	25.6
272	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}, \text{Na}_2\text{B}_4\text{O}_7 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$	0.03	25.5	25.53
...	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$	2.9	1.17	4.07
273	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}, \text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$	11.2	0.2	11.4
278	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}, \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	12.8	4.9	0.3	...	18.0
...	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}, \text{Na}_2\text{B}_4\text{O}_7 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$	12.5	5.0	1.4	...	18.9
277	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}, \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}, \text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$	3.2	4.5	2.1	...	9.8
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}, \text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$	0.77	...	0.75	5.1	6.62
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}, \text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$	0.12	...	0.5	11.1	11.72
279	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}, \text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$	0.03	...	0.5	25.1	25.63

SYSTEM XXVIII—20° C.
(Diagram 55)

Point	Solid Phases	Mols per 1,000 Mols of Water				
		Na_3PO_4	Na_2HPO_4	$\frac{\text{Na}_2\text{B}_4\text{O}_7}{2}$	$\text{Na}_2\text{B}_2\text{O}_4$	Total
260	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	12.57	12.57
261	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$...	9.75	9.75
262	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	4.46	...	4.46
263	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 8\text{H}_2\text{O}$	35.14	35.14
264	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}, \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	13.5	6.3	19.8
...	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	13.1	2.0	15.1
...	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	2.0	8.2	10.2
265	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}, \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$...	8.5	2.6	...	11.1
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$...	3.3	3.6	...	6.9
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	3.5	0.7	4.2
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	0.9	6.7	7.6
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	0.7	15.5	16.2
266	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}, \text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$	1.0	34.3	35.3
272	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}, \text{Na}_2\text{B}_4\text{O}_7 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$	0.04	34.8	34.84
...	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$	3.2	1.6	4.8
273	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}, \text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$	12.3	0.2	12.5
278	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}, \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	14.1	6.2	0.5	...	20.8
...	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}, \text{Na}_2\text{B}_4\text{O}_7 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$	13.7	6.3	2.6	...	22.6
277	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}, \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}, \text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$	3.5	5.7	3.7	...	12.9
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}, \text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$	0.85	...	1.35	6.95	9.15
...	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}, \text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$	0.13	...	0.84	15.1	16.07
279	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}, \text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$	0.03	...	0.9	34.2	35.13

SYSTEM XXVIII; Na_3PO_4 - Na_2HPO_4 - $\text{Na}_2\text{B}_4\text{O}_7$ - $\text{Na}_2\text{B}_2\text{O}_4$ - H_2O ; 20°C .



o - $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$, Crystallization Starting Point.

277, 278 and 279 - End Points of Crystallization.

DIAGRAM 55.

SYSTEM XXIX *

Trisodium Phosphate, Disodium Phosphate, Sodium Tetraborate,
Sodium Metaborate, Sodium Chloride, Water

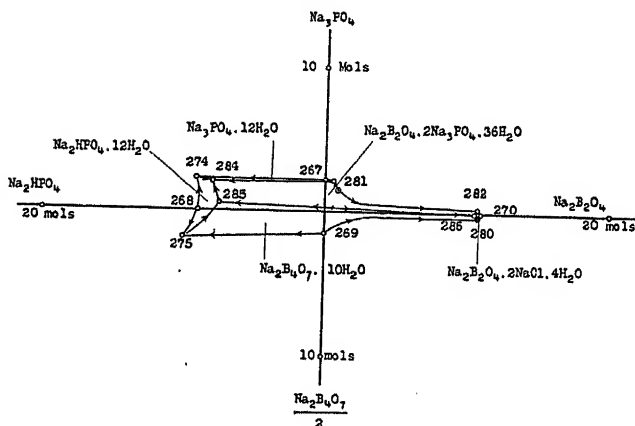
(Diagrams 56, 57)

Systems XXV to XXVIII inclusive have given the four four-component systems leading up to the five-component system, water, the two phosphates, the two borates, and the chloride of sodium. Diagram 56 shows all points saturated with NaCl, and Diagram 57 all points saturated with $\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$; both diagrams drawn to larger scale than we have used heretofore. There are seven possible solid phases here at 20° C., *i.e.*, the five single salts and two double salts, four of these being present at each univariant point, 284, 285, 286, 287, where the solution contains all components, and one or both of the double salts is solid phase at each of these four points.

* Systems XXIX to XXXII inclusive are by W. A. Gale under the direction of William E. Burke.

SYSTEM XXIX; $\text{Na}_3\text{PO}_4 - \text{Na}_2\text{HPO}_4 - \text{Na}_2\text{B}_4\text{O}_7 - \text{Na}_2\text{B}_2\text{O}_4 - \text{NaCl} - \text{H}_2\text{O}$; 20°C .

All points saturated with NaCl.

• - $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$, Crystallization Starting Point.

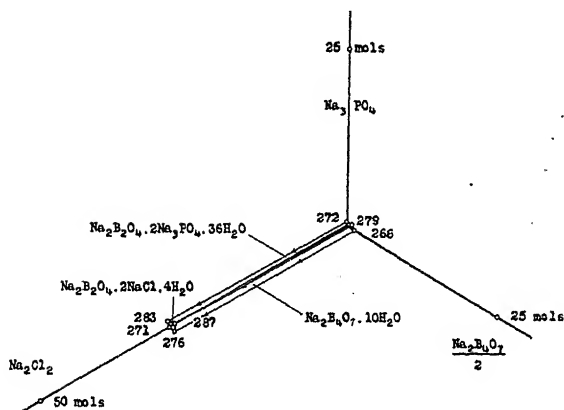
284 and 285 - End Points of Crystallization.

DIAGRAM 56.

SYSTEM XXIX— 20°C .

(Diagrams 56 and 57)

Point	Solid Phases	Grams per 100 Grams of Water					
		Na_3PO_4	Na_2HPO_4	$\text{Na}_2\text{B}_4\text{O}_7$	$\text{Na}_2\text{B}_2\text{O}_4$	NaCl	Total
...	$\text{NaCl}, \text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O},$ $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$	3.1	2.3	0.6	...	33.9	39.9
284	$\text{NaCl}, \text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O},$ $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$	3.2	6.1	0.8	...	32.5	42.6
285	$\text{NaCl}, \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O},$ $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O},$ $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$	2.8	5.9	1.5	...	32.0	42.2
...	$\text{NaCl}, \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O},$ $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$	1.4	...	0.9	1.3	35.3	38.9
...	$\text{NaCl}, \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O},$ $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$	1.7	...	1.0	0.9	35.5	39.1
286	$\text{NaCl}, \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O},$ $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O},$ $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$	0.15	...	0.2	7.6	33.8	41.75
287	$\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}, \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O},$ $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$	0.05	...	0.3	23.0	19.3	42.65

SYSTEM XXIX; $\text{Na}_3\text{PO}_4 - \text{Na}_2\text{HPO}_4 - \text{Na}_2\text{B}_4\text{O}_7 - \text{Na}_2\text{B}_2\text{O}_4 - \text{NaCl} - \text{H}_2\text{O}$; 20°C .All points saturated with $\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$.

287 - End Point of Crystallization.

DIAGRAM 57.

SYSTEM XXIX— 20°C .

(Diagrams 56 and 57)

Point	Solid Phases	Mols per 1,000 Mols of Water					
		Na ₃ PO ₄	Na ₂ HPO ₄	$\frac{\text{Na}_2\text{B}_4\text{O}_7}{2}$	Na ₂ B ₂ O ₄	Na ₂ Cl ₂	Total
...	NaCl, Na ₃ PO ₄ · 12H ₂ O, Na ₂ B ₂ O ₄ · 2Na ₃ PO ₄ · 36H ₂ O	3.4	2.9	1.1	...	52.2	59.6
284	NaCl, Na ₃ PO ₄ · 12H ₂ O, Na ₂ HPO ₄ · 12H ₂ O, Na ₂ B ₂ O ₄ · 2Na ₃ PO ₄ · 36H ₂ O	3.5	7.8	1.4	...	50.1	62.8
285	NaCl, Na ₂ HPO ₄ · 12H ₂ O, Na ₂ B ₄ O ₇ · 10H ₂ O, Na ₂ B ₂ O ₄ · 2Na ₃ PO ₄ · 36H ₂ O	3.1	7.5	2.6	...	49.3	62.5
...	NaCl, Na ₂ B ₄ O ₇ · 10H ₂ O, Na ₂ B ₂ O ₄ · 2Na ₃ PO ₄ · 36H ₂ O	1.6	...	1.5	1.8	54.5	59.4
...	NaCl, Na ₂ B ₄ O ₇ · 10H ₂ O, Na ₂ B ₂ O ₄ · 2Na ₃ PO ₄ · 36H ₂ O	1.9	...	1.9	1.3	54.7	59.8
286	NaCl, Na ₂ B ₄ O ₇ · 10H ₂ O, Na ₂ B ₂ O ₄ · 2Na ₃ PO ₄ · 36H ₂ O	0.16	...	0.4	10.4	52.1	63.06
287	Na ₂ B ₂ O ₄ · 8H ₂ O, Na ₂ B ₄ O ₇ · 10H ₂ O, Na ₂ B ₂ O ₄ · 2Na ₃ PO ₄ · 36H ₂ O	0.05	...	0.5	31.4	29.7	61.65

SYSTEM XXX

Trisodium Phosphate, Disodium Phosphate, Sodium Bicarbonate,
Sodium Carbonate, Sodium Chloride, Water

(Diagram 58)

Water, the two phosphates, carbonate, bicarbonate and chloride of sodium compose a five-component system.

Systems IX and XXV already discussed represent two of the four-component systems which compose System XXX; the others have not been given.

Diagram 58 represents the system at 20° C., all points saturated with NaCl. The two phosphates and the two carbonates are reciprocal salt pairs.

It is very probable that a small field of $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ exists and should be shown at 20° C. (the transition point from the dodecahydrate is given as 19.52°), but the differences of solubility are so slight that for our purpose the possible field has been ignored.

SYSTEM XXX—20° C.

(Diagram 58)

Point	Solid Phases	Grams per 100 Grams of Water					
		Na_3PO_4	Na_2HPO_4	NaHCO_3	Na_2CO_3	NaCl	Total
288	NaCl , $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	2.2	19.0	25.0	46.2
292	NaCl , $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, NaHCO_3	...	6.2	1.4	...	32.2	39.8
297	NaCl , $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, trona	2.4	...	0.8	18.5	24.9	46.6
298	NaCl , $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, trona, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	9.7	1.4	5.1	...	29.0	45.2
299	NaCl , NaHCO_3 , $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, trona	8.3	2.1	4.9	...	29.7	45.0

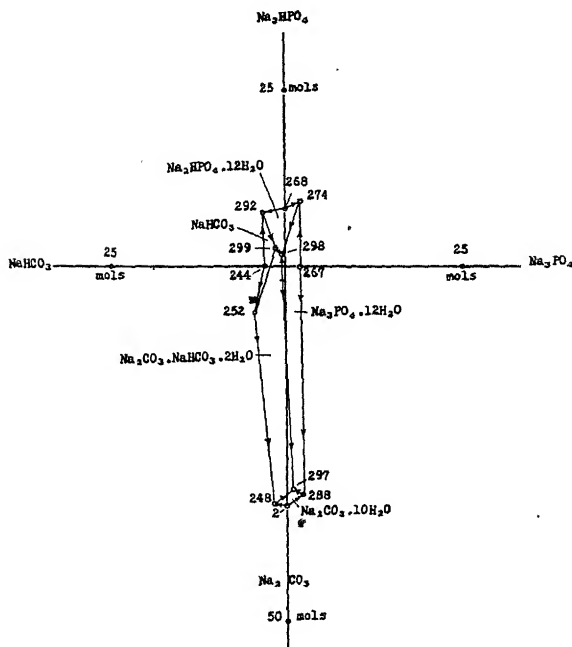
SYSTEM XXX—20° C.

(Diagram 58)

Point	Solid Phases	Mols per 1,000 Mols of Water					
		Na_3PO_4	Na_2HPO_4	NaHCO_3	Na_2CO_3	Na_2Cl_2	Total
288	NaCl , $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	2.4	32.3	38.5	73.2
292	NaCl , $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, NaHCO_3	...	7.8	3.0	...	49.7	60.5
297	NaCl , $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, trona	2.7	...	1.7	31.4	38.4	74.2
298	NaCl , $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, trona, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	10.6	1.8	10.9	...	44.7	68.0
299	NaCl , NaHCO_3 , $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, trona	9.1	2.6	10.5	...	45.7	67.9

System XXX - Na_3PO_4 - Na_2HPO_4 - NaHCO_3 - Na_2CO_3 - NaCl - H_2O - 20°C .

All Points Saturated with NaCl .



□ - $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ Crystallization Starting Point.

297 - 298 - End Points of Crystallization.

DIAGRAM 58.

SYSTEM XXXI

Sodium Bicarbonate, Sodium Tetraborate, Disodium Phosphate,
Sodium Chloride, Water

(Diagram 59)

Water and the acid carbonate, acid borate, acid phosphate, and chloride of sodium compose a five-component system with no reciprocal salt pairs. Systems VIII and XXVI are two of the four-component systems composing this one.

SYSTEM XXXI—20° C.

(Diagram 59)

Point	Solid Phases	Grams per 100 Grams of Water				
		NaHCO ₃	Na ₂ B ₄ O ₇	Na ₂ HPO ₄	NaCl	Total
291	NaCl, NaHCO ₃ , Na ₂ B ₄ O ₇ ·10H ₂ O	0.9	1.0	...	34.5	36.4
292	NaCl, NaHCO ₃ , Na ₂ HPO ₄ ·12H ₂ O	1.4	...	6.2	32.2	39.8
275	NaCl, Na ₂ HPO ₄ ·12H ₂ O, Na ₂ B ₄ O ₇ ·10H ₂ O	...	1.0	7.8	32.5	41.3
296	NaCl, NaHCO ₃ , Na ₂ B ₄ O ₇ ·10H ₂ O, Na ₂ HPO ₄ ·12H ₂ O	1.4	0.4	8.0	31.3	41.1

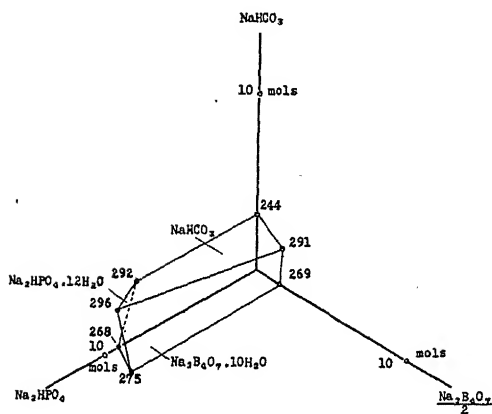
SYSTEM XXXI—20° C.

(Diagram 59)

Point	Solid Phases	Mols per 1,000 Mols of Water				
		NaHCO ₃	$\frac{Na_2B_4O_7}{2}$	Na ₂ HPO ₄	Na ₂ Cl ₂	Total
291	NaCl, NaHCO ₃ , Na ₂ B ₄ O ₇ ·10H ₂ O	2.0	1.7	...	53.2	56.9
292	NaCl, NaHCO ₃ , Na ₂ HPO ₄ ·12H ₂ O	3.0	...	7.8	49.7	60.5
275	NaCl, Na ₂ HPO ₄ ·12H ₂ O, Na ₂ B ₄ O ₇ ·10H ₂ O	...	1.8	9.9	50.1	61.8
296	NaCl, NaHCO ₃ , Na ₂ B ₄ O ₇ ·10H ₂ O, Na ₂ HPO ₄ ·12H ₂ O	3.1	0.8	10.1	48.3	62.3

System XXI - NaHCO_3 - $\text{Na}_2\text{B}_4\text{O}_7$ - Na_2HPO_4 - NaCl - H_2O - 20°C .

All Points Saturated with NaCl.



296 - End Point of Crystallization.

DIAGRAM 59.

SYSTEM XXXII

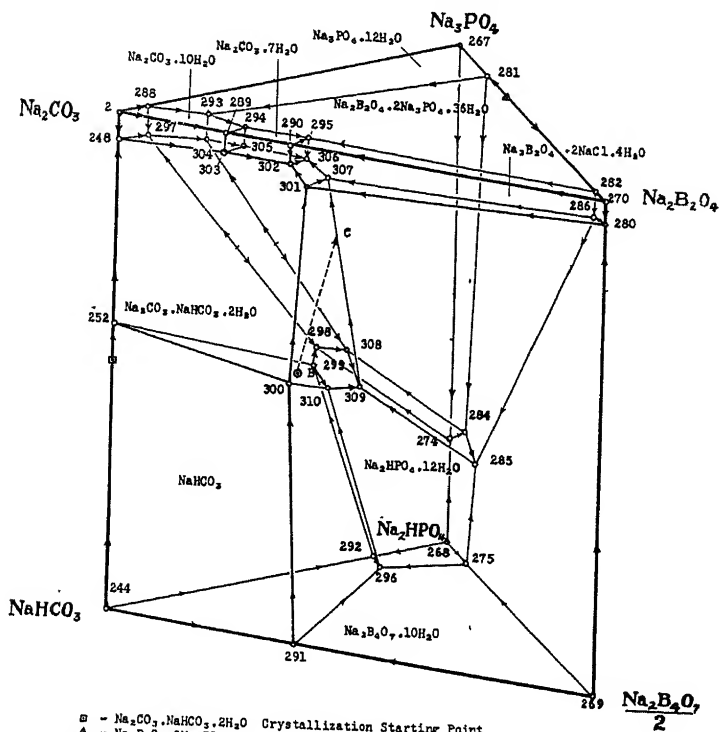
Trisodium Phosphate, Disodium Phosphate, Sodium Carbonate, Sodium Bicarbonate, Sodium Metaborate, Sodium Tetraborate,
Sodium Chloride, Water

(Diagram 60)

Finally in Diagram 60 an attempt is made to give some sort of picture of a six-component system. It is probably more illustrative than instructive. We have water and seven sodium salts, the chloride, tri- and disodium phosphates, carbonate and bicarbonate, borate and metaborate. Omitting chloride for the moment we may consider the other components to be the three radicals $-\text{CO}_3$, $-\text{B}_2\text{O}_4$, and $-\text{NaPO}_4$ combined with two other radicals $-\text{Na}_2$ and $-\text{NaH}$. In the upper triangle of Diagram 60 each vertex represents saturation with NaCl and one of the three radicals combined with Na_2 . Other points in the triangle are plotted in molecular proportions of the three radicals present. Each vertex of the lower triangle of the prism likewise represents saturation with NaCl and one of the same three radicals combined with NaH. Points between the two triangles showing ratio of Na_2 to NaH are plotted on the vertical axis showing the proportion of the three radicals present. The whole forms, of course, a triangular prism. Points 289, 293, 294, 295 and 303 to 310 inclusive have not been accurately determined, but are shown in their probable positions.

Although this system contains seven sodium salts it lacks two important constituents of lake brine, potassium and sulfate, and so again we have only a partial picture. With these omissions the composition of lake brine is represented by point B in Diagram 60, saturated with NaCl, trona and borax, and nearly saturated with bicarbonate. Isothermal evaporation at 20°C . would cause the concentration to change in the direction of the line B-C, precipitating chloride, trona and borax. At point C the phosphate metaborate double salt would start to precipitate also. Further evaporation would lead to point 307, all four salts being precipitated en route, and at point 307 a fifth one, the chloride metaborate double salt, begins to precipitate. Still further evaporation leads to point 306, the end point of crystallization, where sodium carbonate precipitates and borax is no longer in stable equilibrium. If we add KCl and glaserite to the five solid phases present at point 306 we should expect to reproduce the situation that will arise if and when the lake should become nearly dry. Experiments on natural brine indicate that this is correct, and the above seven solid phases would be present.

System XXXII - Na_3PO_4 - NaHPO_4 - Na_2CO_3 - NaHCO_3 - $\text{Na}_2\text{B}_2\text{O}_7$ - $\text{Na}_2\text{B}_4\text{O}_7$ - NaCl - H_2O - 20°C .
All Points Saturated with NaCl .



- - $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ Crystallization Starting Point.
 ▲ - $\text{Na}_2\text{B}_2\text{O}_7 \cdot 2\text{Na}_2\text{PO}_4 \cdot 36\text{H}_2\text{O}$ Crystallization Starting Point.
 207 - $\text{Na}_2\text{B}_2\text{O}_7 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$ Crystallization Starting Point.
 ⊙ B - Searles Lake Brine.
 306 - End Point of Crystallization.

DIAGRAM 60.

This concludes the presentation of equilibrium diagrams and data. There will be found included sixteen systems of two components, thirty-eight of three components, twenty-five of four components, six of five components, and one of six components, one component always being water. Some systems are given at a single temperature, others at four or five temperatures over a considerable range. This obviously does not exhaust the subject; far from it. Only those are given which we found it necessary to work out for our own purposes, and naturally not all of those.

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